

Laser modification of the materials surface layer – a review paper

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Abstract. The state of laser processing in surface materials modification in Poland is reported, based on own experience, coworkers and coauthors results, as well the literature review. The curriculum concerning historical development of lasers and laser technology in Poland, laser-matter interaction, as well basis of different laser techniques applied in materials surface engineering (solid state hardening, melting, alloying, cladding, ablation, shot peening, cleaning and texturing) are reviewed, and compared with results of coauthors, as well with a wide range of Polish authors papers. Finally, it is concluded that overall state of research on laser application in surface engineering in Poland is well developed and still growing industrial application is observed.

Key words: lasers in Poland, laser surface heat treatment, laser melting, alloying, cladding, laser ablation, laser cleaning, laser shock processing, laser texturing, multilayer coatings.

1. Introduction

Lasers have enormously provided to important fields of science as well as technologies since T. Maiman [1] in 1960, created the first working ruby laser. Just after his invention the first applications of ruby lasers took place in USA, in drilling diamonds for wire draw dies.

Also Polish researchers were very active in development of laser technology. Three years after Maiman had built his ruby laser, Polish researchers constructed first He:Ne gas lasers: at the Military University of Technology, at Warsaw Technical University, as well at University of Adam Mickiewicz in Poznan. In 1965, on the base of the ruby laser, the first micro drilling machine was constructed at the Military University of Technology. At the same time, at the Warsaw Technical University the micro drilling-welding machine equipped with the neodymium glass laser was built up (in the next years they constructed also the drilling machines operating with Nd:YAG pulsed laser and with Nd:YAG CW laser, as well with Nd:YAG pulsed laser of high frequency). During 1970s several papers and books concerning interaction of laser with the matter were published in Poland.

The papers published by Paszkowski, Wolinski and Nowicki [2] on: "Some problems of laser beam welding and drilling", Puzewicz and Slojewski [3] on: "Laser processing of formed holes" as well: Wolinski and Nowicki [4] on "Laser treatment of materials", and the books on: "The laser in materials processing and metrology" written in 1973 by Sadowski and Krehlik [5], as well Nowicki [6] on: "Lasers in electronic technology and in materials treatment", are one of the first Polish publications concerning interaction of lasers with materials. Zimny [7] conducted one of the first in Poland complex

studies on materials laser drilling. His investigations on laser beam machining are summarized in the habilitation thesis [8].

Kusinski [9] started to investigate laser heat treatment of materials in 1971 during realization of PhD thesis on "Effect of the heating rate, time and temperature on the hypereutectoid tool steels homogeneity". The Nd:YAG, laser working at the Institute of Metal Cutting in Krakow (now: The Institute of Advanced Manufacturing Technology), was used as the one of the heat sources applied for the rapid heating of tool steel samples. The main achievement of these studies was detailed analysis of structural and compositional (using SEM, TEM, XRD and microprobe techniques) changes involved in the surface layer of tool steels by a pulsed laser. Kusinski [9] showed the significant structural refinement and high level of the chemical homogeneity of laser-melted layer. In the case of laser hardening without melting and in the heat affected zone (just beneath the melted zone) residues of un-dissolved carbides were still present in the structure causing higher structural and compositional inhomogeneity. Indeed non uniform hardness values were measured in such zones. This finding permitted to conclude that for the laser solid state hardening the initial tool steel structure should be highly homogeneous. The best would be tempered martensite or bainitic structures.

The successful experimental studies of Polish researchers on laser-induced material processing have been reported since the end of 1970s [10–18]. The experiments were based on the use of Nd:YAG and CO₂ lasers in hardening, melting and alloying of steels and cast irons.

Actually in Poland, the research on laser beam application to materials processing is running in many laboratories located at universities, scientific institutes and in industries

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throughout the country. The much more active research teams are located at several Polish Universities of Technology (Warsaw, Warsaw Military, Cracow, Kielce, Rzeszow, Poznan, Silesian, Lodz, Wroclaw) as well AGH University of Science and Technology – Cracow, West Pomeranian University of Technology – Szczecin, University of Warmia and Mazury – Olsztyn: institutes of the Polish Academy of Sciences: Institute of Metallurgy and Materials Science, Institute of Fundamental Technological Research – Warsaw, Institute of Fluid-Flow Machinery – Gdansk; research institutes: Welding Institute of Gliwice, Institute of Advanced Manufacturing Technology – Cracow, Institute of Electron Technology – Warsaw, and many others. The practical laser processing (cutting) has been used since the 1990's. The growth of industrial application of the laser cutting, drilling and welding expanded very rapidly in Poland at the end of 1990's and at the beginning of 2000's. Nowadays, when traveling through Poland, one can meet thousands of boards advertising the laser cutting, drilling and welding processes offered by small and medium companies.

Nowadays, the units offered by the laser manufacturers, can deliver beam with wavelength in the range from the ultraviolet (UV) to infrared radiation, and with high continuous or pulsed power density (beam power may vary from very low (\sim mW) to extremely high (1–100 kW)), with spatial, as well as, temporal coherence, low divergence, and monochromaticity [19–21]. At present, it is hard to imagine the human life in the developed countries without using laser light! The applications of lasers include: communication, metrology, reprography, entertainment, military, chemical, medical, heat source (materials processing). Laser materials processing include: cutting, drilling, welding, surface hardening, alloying, cladding, rapid prototyping, laser-assisted forming (bending), ablation and shot peening.

During laser materials processing, the laser light (from a pulsed or continuous wave laser beam) strikes the surface of material, but due to high reflectivity of majority materials to laser radiation a portion of beam energy is reflected from the material surface, while the rest is transferred into the material. Conversion of the absorbed energy to heat involves: excitation of valence and/or conduction band electrons, excited electron-phonon interaction within 10^{-11} – 10^{-12} s, electron-electron or electron-plasma interaction and electron-hole recombination within 10^{-9} – 10^{-10} s [22, 23].

Therefore, it can be assumed that the process of energy deposition from a pulsed/continuous wave (CW) laser beam into the near surface region of a solid involves electronic excitation and relaxation within an extremely short period of time in ultra-thin layer. In other words, the laser–matter interaction within the near surface region achieves extreme heating and cooling rates (10^3 – 10^{10} K s⁻¹), while the total deposited energy (typically 10^3 – 10^4 J cm⁻²) is insufficient to affect, in a significant way, the temperature of the bulk material [22–25]. This permits the near surface region to be processed under extreme conditions introducing only a tiny effect on the bulk properties.

Absorption of the laser radiation on the surface generates heat and after the laser pulse stop or beam displacement to

another area, the material is quenched by heat transportation inside. In the simplest way, the temperature field in the laser treated material can be described by the standard heat conduction equation. The modeling of the laser heating process offers better understanding of the laser processing of engineering materials, indeed considerable research studies were carried out to understand the laser pulse/continuous heating process in the thin surface layer. Several researchers investigated the modeling of temperature distribution induced by the laser radiation in solids for the stationary beam and for the moving beam interaction. The calculated temperature distribution inside the target as a function of time was presented by Ready [24] and Rimini [25]. Yilbas et al. [26] examined the laser heating mechanism including the evaporation process. They formulated the drilling efficiency and showed that at high-intensity beams, the temperature inside the material rises from the surface to a maximum at some point below the surface before decaying to zero at infinity.

Also Polish researchers studied the laser beam/matter interactions and calculated a temperature field in the treated material. Studies of laser-matter interaction modeling one may find in papers of Nowicki [6], Zimny [7], Domanski [27], Parkitny et al. [28] and Marczak et al. [29]. In the model, basing on the hydrodynamic equations for continuous medium, Marczak et al. [29] took into account the absorption of laser radiation, ionization of the medium, thermal conductivity, shock-waves and elastic medium characteristics. On the other hand, the phase transitions (melting, vaporization) were not considered. Therefore, the analysis of interaction of laser radiation with the target is, so-called “not-threshold” and the final results are only qualitative.

Effect of materials heating with the laser radiation depends on thermal balance of surface absorbed laser energy and thermal energy transferred to the “cold” material. With the rate of laser energy deposition much higher than the rate of heat transfer to the core material the high temperature is localized in the thin surface layer. When both rates (heat absorption and diffusive transport) are equal the material is heated to lower temperature and thicker surface layer is heated.

Figure 1 presents a brief overview of the application of laser in the different laser surface technologies [22]. For each of these types of laser surface processing the laser power/energy density and interaction/pulse time must be properly selected in terms of achieving the desired degree of heating and phase transition.

Laser materials processing can mainly be carried out in three ways:

- without melting (transformation hardening, bending and magnetic domain control – processes require low power density);
- with melting (surface melting, glazing, cladding, welding and cutting – processes require high power density);
- with vaporization (cutting, drilling, ablation – processes require substantially high power density within a very short interaction/pulse time).

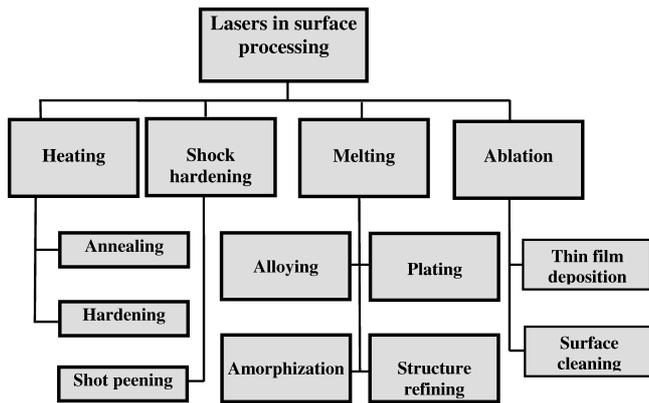


Fig. 1. Spectrum of laser applications in surface processing

One of the major advantages of the laser materials processing is the possibility of accurate control the area where laser radiation should be delivered, as well the amount and rate of energy deposition. Only the amount of the laser beam energy that is absorbed by the material can contribute to processes like heating and melting. The specific properties of laser beam that enable and justify their use in such a wide spectrum of applications are: spatial and temporal coherence (i.e. phase and amplitude are unique), low divergence (parallel to the optical axis), high continuous or pulsed power density and monochromaticity.

The use of laser science and technology in the development of materials made significant progress due to the flexibility of control of the beam's interaction, with regard to wavelength, energy density and interaction time, and the wide choice of interaction environments.

It is difficult to think of any field of science where lasers have not left their mark in improving material properties and behavior, or in widening material applications. Some laser processes like surface annealing, do not demand high density of laser beam energy. However, surface melting, glazing, cladding and welding that involve melting require high laser power density to induce the change in state and phase transformation in large volume/area. Moreover, processes like cutting, drilling and similar machining operations that remove material as vapor, need delivery of a substantially high power density within a very short interaction/pulse time.

2. Laser surface processing techniques

2.1. Laser surface heat treatment. In general, heat treatment means the controlled heating and cooling of metallic materials to alter their physical and mechanical properties without changing the product shape and is often associated with the increasing strength of materials. Surface transformation hardening of ferrous materials using lasers typically is performed to improve wear characteristics, as well fatigue properties machinery elements (ex. shafts, gear teeth, etc.).

The important processing parameters for the laser surface heat treatment include the laser beam power, focused laser beam diameter, distribution of power (or heat intensity distribution) across the beam, absorptivity of the beam energy by the treated material surface, scanning velocity of the laser

beam across the substrate surface, and the thermal properties of the treated material. Since the laser beam is finite in size, the process is ideally suited to perform specific localized area treatment. The laser heat-treating typically is performed without the use of an external quenching, indeed the experienced role is that the case depth-to-section depth ratio should be approximately 1:7–10 for the self-quenching of most materials. To date, considerable amount of research has been done concerning the laser hardening of ferrous alloys (steels and cast irons).

Steen and Courtney [3] conducted a comprehensive investigation of laser transformation hardening of an AISI 1036 steel using a 2 kW continuous wave CO₂ laser and concluded that the depth of hardening is a function of the parameter $P = (D_b V)^{1/2}$ and the onset of surface melting as a function of the parameter $P = D_b^2 V$ (where: D_b – beam diameter and V – scanning velocity).

Ashby and Easterling [31] as well as Li et al. [32] investigated transformation hardening of hypo- and hypereutectoid steels, respectively, using a scanning laser beam. Two continuous wave CO₂ lasers (0.5 and 2.5 kW) were used in these studies. The beam diameter was varied from 1 to 10 mm and the beam velocities in the range of 2–30 mm/s. They considered both Gaussian as well as “top hat” or uniform energy density distributions.

Ashby and Easterling [31] for the modeling of laser hardening of hypoeutectoid steel combined approximate solutions to the equations of heat flow with the kinetic models to predict the near surface structure and hardness of plain carbon steels. One-dimensional heat flow model with approximate formulas was used for the calculation of the thermal field. The kinetic models employed included equations for the conversion of pearlite and ferrite to austenite, subsequent homogenization in austenite, and final quenching to martensite. The mathematical model and computer programs can be used to optimize scanning speed and other laser processing parameters. As can be expected, the profile produced by the “top hat” was more uniform than that of the Gaussian beam. The Authors [31] developed approximate solutions for the heat flow and combined them with the kinetic models to predict the microstructure and hardness variations with depth from the surface due to laser transformation hardening. The obtained diagrams showed the combination of process variables, such as energy density, beam radius, and depth below the surface for a given microstructure and the associated hardness profile.

Cline and Anthony [33] conducted one of the first comprehensive thermal analysis of the laser heat treatment with a scanning laser beam using a circular (or disc shaped) moving heat source with a Gaussian distribution of heat intensity under quasi-steady-state conditions.

Most of the mathematical models proposed by these researchers are based on the solution of the conventional heat conduction equation. Anthony and Cline [34] performed the first quantitative work and proposed the theory and mathematical model for the laser heating and melting with a Gaussian beam that moves at a constant velocity. They correlated the temperature distribution and the depth of the melting with the

size, velocity and the power level of the beam. Chan et al. [35] considered a two-dimensional transient model of laser melting. Movement of the heat source was taken into consideration by coordinate transformation. Many studies were performed for theoretical analysis of laser surface treatment process using the finite element analysis for calculation of a temperature field in metals that are irradiated with laser during heating and melting processes [36].

In practice, since the laser hardening process is strongly dependent on absorbed laser beam energy, it is very hard to realize a pure laser solid-state hardening of steels and other materials without melting of a surface layer. Each imperfection at the surface of the laser treated material, by changing the surface absorption coefficient to laser light, may cause differences of absorbed laser beam energy value, especially in the case of multi-pass heating of large surface with heating tracks overlapping. Indeed, more popular and technically easier is the laser hardening with melting of thin surface layer. Moreover, the melting and subsequent rapid solidification provide chemical homogenization of the melted zone and structural refinement.

Kusinski and Thomas [37] studied the details of austenite transformation during laser heating of two grades of chromium steels (containing 3 and 10% Cr), because the austenitizing process during laser hardening affects the types and properties of the subsequent martensitic structures. They used a 1250 kW CO₂ laser with cylindrical lens producing a narrow-elliptical spot and three scanning velocities (4.23, 6.33 and 8.46 mm/s).

The surface-layers obtained with using lower scanning velocity (longer laser beam-material interaction time) heating show three marked zones: deep or shallow melted (MZ) – in the case when material was heated above the solidus; hardened zone (HAZ) – material heated to the austenitizing range and tempered zone (TZ) – material heated below the austenitizing range. The surface layers formed during laser treatment with the highest scanning velocity contain only two zones: hardened (HZ) and tempered (TZ). It was shown that, using constant energy density depending on interaction time, the laser beam might produce both thermal melting and only heating. In both cases of laser melting (shallow and deep melting) laser melting produced a marked refinement in the scale of the dendritic microstructure corresponding to the cooling rate. Moreover, there is a strong tendency for the epitaxial growth on the substrate and an effect of “shape memory” to the primary grains. The martensitic laths have frequently the same orientation in both the resolidified and un-melted parts of the grains. This indicates that the newly solidified crystals that grow epitaxially from the un-melted parts of grains have the same crystallographic orientation. The grains formed in the melted zone are very large, but they have the substructure of the fine cellular grains that determines the martensite packet size in this zone. The grain size of HAZ (below MZ) depends on the austenitizing temperature reached during heating. The region just below MZ is where the highest temperature was reached is composed of the characteristic, coarse and irregular grains. The grains in the central region of HAZ have a very fine (of about 8–10 μm) irregular na-

ture. The internal structure of these grains is a very fine martensite. Laser heating with 8.46 mm/s scanning velocity results in a hardened layer of material with higher wear resistance (1.4–1.6 times better) than that for conventionally hardened steels. Both the melted and heat affected zones have higher hardness than the substrate. The microstructures produced were essentially packet martensite (dislocated and fine twinned laths surrounded by retained austenite films). The austenite-grain refinement caused by the rapid laser heating and high stresses induced during cooling creates a refined packet structure of laths and retained austenite films. The examinations showed that the heating and quench rates, and thus resulting chromium steel structure and properties, can be precisely controlled by adjusting laser parameters such as scan speed for CW lasers and intensity. For example, back tempering can occur when the scanning laser beam overlaps an area previously processed, causing it to again reach the tempering temperature range. The result is that the overlapped area can have lower hardness than the rest of the hardened zone.

Kusinski and Thomas [37] concluded that since the improvement in wear resistance is higher than that of hardness, toughness and compressive stresses are also factors that determine abrasive wear resistance of these steels.

Kusinski et al. [38] studied the structure, chemical composition and properties (hardness and wear resistance) of 30CrMnMo16-8 constructional steel after pulsed laser treatment by using the high power CO₂ laser. Material was investigated in order to get better understanding of the essence of laser hardening of this steel grade. Application of advanced analytical techniques (scanning and transmission electron microscopy, and EDS microchemical analysis) permitted to analyze structural details the laser hardened layer, as well as to show fine differences in comparison with the conventionally hardened steel. The examinations showed that microstructure produced in the laser hardened layer was essentially packet martensite (dislocated and fine twinned laths), while coarser lath martensite was present in the matrix. It was shown, that high wear resistance of the laser hardened steel was not only due to grain refinement caused by rapid laser heating but also high stresses induced during rapid cooling of the surface layer, both creating essentially fine, highly dislocated and internally twinned martensite with some amount of stable, interlath retained austenite.

Bylica and Adamiak [39] studied the influence of laser beam hardening and tempering of carbon steels (15, 45 and N9E) on the structure, microhardness and abrasion resistance and demonstrated that remelting of steel with laser beam changes significantly the properties of surface layers. In laser-remelted layer of steel 15 lath martensite was identified, while in 45 and N9E plate martensite with some amount (higher in case of N9E steel) of retained austenite. The highest hardness (micro Vickers Hardness) over 1000 μHV was measured in the heat affected zones which was much higher than in the laser remelted zone (700–800 μHV). It was shown that abrasive resistance of laser-hardened samples was about 6 times higher than that of normalized samples.

Molian and Baldwin [40] in their work on pin-on-disk wear behavior of laser hardened gray and ductile cast iron found that sliding wear resistance increased with an increase in case depth. Chen et al. [41] studied the details of austenite transformation during laser heating, because the austenitizing process during laser hardening affects the types and properties of the subsequent martensitic structures. The Authors concluded that in the case of laser high heating rate, (when the super-heating degree is very high) non-diffusive transformation $\alpha \rightarrow \gamma$ occurs, indeed the austenite can form crystals not only at the ferrite grain boundaries but also in grain interior at any place where the energy enhancement exists.

The laser surface hardening consists of the rapid heating of a materials surface by the laser beam, a short holding at the target temperature, and intensive cooling due to the high thermal conductivity of the material. The surface may not melt up. The hardening depth is limited to approx. 1 to max. 1.5 mm beneath the surface by the heat conductivity and self-quenching. Mainly the spot geometry of the laser at the processing spot and the feed rate determine the temperature pattern. Compared to other lasers used for hardening (CO_2 and Nd:YAG) lasers, diode lasers have the advantage of a shorter emission wavelength (808 nm or/and 940 nm) that is better absorbed by metals (the usual black painting does not apply), and superior process stability. Additionally, diode lasers do not require special absorption layers that can prevent temperature control by a pyrometer and also may result in the contamination of the surface. Due to the high efficiency of the diode laser, as well its beam profile, lower investment and running costs, as compared to the Nd:YAG laser, they are preferentially used in materials surface hardening.

A unique advantage of the diode laser hardening process over conventional heat treating processes is the possibility to adjust its spot ideally to the contour requiring hardening and, therefore, to achieve extremely high throughput.

2.2. Laser melting. Laser melting of metallic substrates finds wide application in industry due to their precision of operation and production of a fusion zone with high depth/width ratios, minimizing the total amount of material affected or distorted by a laser beam. The absorbed high-energy beam results in a rapid rise of substrate temperature. If the beam intensity is high enough, the increasing surface temperature can exceed the melting point of the substrate material. Then melt is formed on the surface. The front between the liquid and solid phases propagates inside the material as the heat is conducted from the surface into the material bulk, and the surface temperature increases until heat conduction and the heats of melting and evaporation balance the surface energy deposition.

The principal aim of use *laser melting* technique in the material surface processing is to improve their properties such as wear, erosive and corrosive resistances due to formation of hard, homogenous and ultrafine structure of the material surface layer, without changing its chemical composition. Metallurgical changes that occur in the laser melted surface layer are in the form of grain refinement, supersaturated solid

solutions, and fine dispersions of particles. All these fetches can contribute to the hardening and strengthening of the surface layer. The laser melting can harden alloys that cannot be hardened so effectively by the laser transformation hardening. The good examples are cast irons and alloyed steels containing carbide-forming elements (W, Mo, V, etc.) i.e. high-speed tool steels. During laser transformation hardening of such materials, due to usually short interaction time between the laser beam and treated material, carbides are unable to be dissolved in austenite to saturate it sufficiently with carbon and alloying elements. So, the material cannot get high hardness level. For this reason, the technique of laser surface melting of such materials found many practical applications, as a method of formation of rapidly resolidified surface layers, possessing many advantageous properties. Up to now, the laser surface melting of high-speed tool steels was examined by many authors [12, 42–47]. In Poland, one of the earliest investigations of the HS 6-5-2 steel laser surface melted was performed by Straus and Szylar [43]. The Authors applied variable treatments, in which the laser surface melting was used after or before conventional hardening and tempering treatments. The laser treatment of high-speed tool steels was also subject of extensive research conducted by Bylica et al. [46, 47]. The Authors shown advantageous influence of Nd:YAG pulsed laser surface melting and post laser tempering on the cutting properties of the indexable inserts. They showed about 60% improvement of cutting tools lifetime. The less effective results they obtained when CO_2 CW laser was used to melt the surface layer of cutting tools. Such difference was explained as the result of differences in microstructure. In the case of pulsed laser melting the microstructure was more refined than after CO_2 CW laser treatment. Also the dendrite axes were differently oriented in the surface melted layer. In the case of Nd:YAG pulsed laser melted layer they were perpendicular to the cutting surface. Our examinations [12, 45, 48] indicate, that the initial structure of steel does not influence too much microstructure of the surface layers forming during its laser re-solidification. Only in the case of steels having very large carbide particles in the matrix un-dissolved carbides are still observed in the resolidified layer.

Recently, Jaglarz and Grabowski [49] have investigated the AlSi/SiC composite materials before and after laser melting. They showed that after laser remelting SiC particles were distributed unevenly in the ultrafine eutectic structure of Al-Si alloys. The hardness of the laser remelted layer ($\sim 110 \mu\text{HV}0.05$) was higher than untreated matrix ($\sim 75 \mu\text{HV}0.05$).

Kusinski et al. [50] studied the microstructure and properties of Nd:YAG laser remelted iron base $\text{Fe}_{57}\text{Cr}_8\text{Mo}_{12}\text{W}_3\text{C}_9\text{B}_{11}$ amorphous coatings. The goal of the research was to increase the wear resistance of items made of high strength 9%Cr steel by post-spray laser melting of HVOF-sprayed $\text{Fe}_{57}\text{Cr}_8\text{Mo}_{12}\text{W}_3\text{C}_9\text{B}_{11}$ amorphous alloy coatings. The coatings were laser remelted with certain portion of matrix in order to receive amorphous microstructure of the surface layer, free of porosity and well metallurgically bonded with the matrix. The Authors showed that by changing the laser melting process parameters it was possible to control

the chemical composition, microstructure and properties of remelted samples. The microstructure of as deposited coatings and laser remelted surface layer was investigated by means of X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). It is clearly visible that laser remelting of HVOF sprayed coating and thin layer of substrate permitted to get very good metallurgical bonding between remelted layer and substrate, much better than that between HVOF sprayed coating and substrate. The investigation showed that using proper laser treatment conditions of coating remelting, it is possible to get amorphous or nanocrystalline surface layer, with high hardness ($\sim 1650 \mu\text{HV}$) and wear resistance (two times better sliding wear resistance than as sprayed coatings), however with presence of cracks.

2.3. Laser alloying. Laser alloying of surfaces with selective alloying elements, which started as early as 1964 [51], is now a well developed surface engineering process, widely described in the literature. The potential of surface alloying to reduce consumption of expensive alloying elements is both strategically and commercially significant [52, 53]. The process of laser surface alloying (LSA) is similar to the surface melting with the laser; however, to modify the surface chemical composition, a desired alloying element should be added to the melt pool. The technique has become more and more popular, since there are several different ways of introducing the alloying element into the thin surface layer melted by the laser beam [44]. These include direct injection (see Fig. 2) into the melt pool at time of the treatment (powder, wire, gas), preplaced adherent coatings (see Fig. 3) deposited prior to laser treatment (electroplating, diffusion coating, thermal spraying, sputtering, etc.), and preplaced non-adherent coatings (foils, pastes, powder slurries). During the laser beam interaction with die sample's surface the preplaced layer and the substrate are melted and both liquids are intensively mixed and consequently during the solidification a new desirable surface alloy is formed. The role of the shear stress is particularly important since it influences the convective movement and, consequently, the distribution of the alloying elements in the molten pool. The intensity of the convective movement in the melted pool and, hence, the velocity of liquid transport is also highly influenced by the temperature gradient [44, 54]. Generally, the temperature gradient increases with the increasing laser energy input during unit time. The additional parameter that strongly influences the mixing of material species in the melted pool is the sign of the temperature gradient at the surface [55]. For the multimode energy distribution in the laser beam, the sign of the temperature gradient changes several times, creating few opposite vortexes in the liquid and consequently a multidirectional mass and heat transport.

In the past years several Polish researchers studied laser alloying process. Between many papers the most interesting were published by scientists from AGH [55–59], as well Gliwice [60–63], Rzeszow [63, 64] and Poznan [65–68] Universities of Technology.

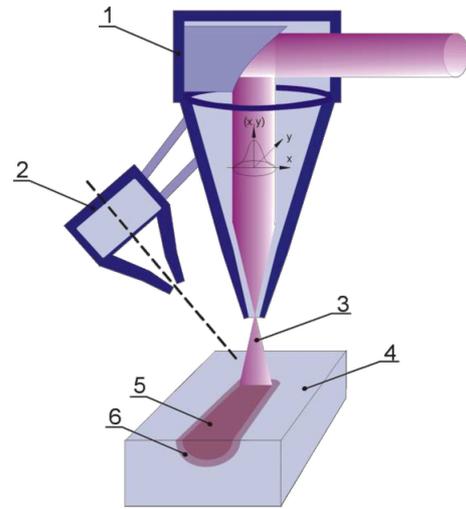


Fig. 2. Principle of laser alloying with direct powder injection into the melted pool; 1 – focusing optic, 2 – powder supply, 3 – laser beam, 4 – material, 5 – alloyed zone, 6 – heat affected zone

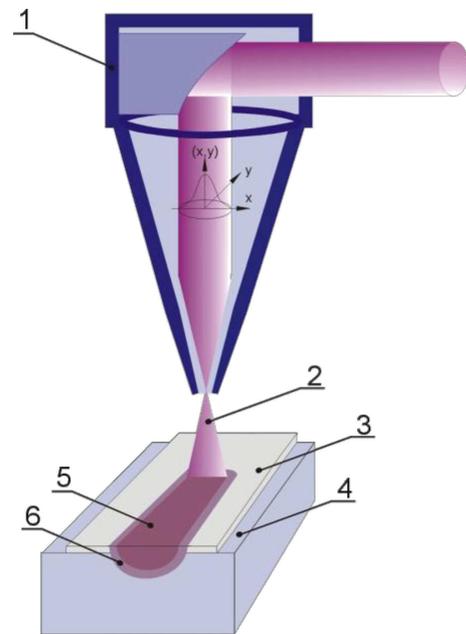


Fig. 3. Principle of laser alloying with preplaced adherent coating; 1 – focusing optic, 2 – laser beam, 3 – preplaced coating of alloy material, 4 – material, 5 – alloyed zone, 6 – heat affected zone

Didenko et al. [55–57] studied in details the laser alloying process of high purity iron with $40 \mu\text{m}$ Cr electrolytically predeposited on the sample surface. The Authors have used the CW CO_2 laser generating TEM_{10} Gaussian mode with an output power of 2 kW and 2.5 kW focused to the diameter of 3 mm and constant speed of the work table set to 18.4 mm/s. The process was carried out in an argon atmosphere. For the process modeling a multiphase mathematical model of the laser re-melting of high purity iron with a pre-deposited chromium layer was used resulting from solution of the partial differential equations for conservation of energy, mass and momentum. The FLUENT program was used for numerical modeling of the fluid flow and mass transfer in the molten

pool during laser alloying. Finite element mesh used to simulate alloying process was prepared with the GAMBIT program. The numerical results, predicting the final composition in the solidified alloy, Didenko et. al [55–57] compared with corresponding experimental results and the agreement they found to be good. The non-uniform chromium distribution (the presence of high chromium concentration fields near the solid/liquid interface) is caused by a multidirectional liquid material movement, which is due to the presence of a few vortices in the melted pool. The presence of vortices in the liquid is caused by the non-uniform energy distribution in the laser beam (TEM₁₀ mode), which directly influences the mass transport kinetics and gives rise to the final dimension and shape of the melted pool, its microstructure and, consequently, properties of the resolidified material.

Dobrzanski et al. [60] studied process of alloying of X40CrMoV5-1 steel surface layer with tungsten carbide by the use of a high power diode laser. The Authors tried to determine the technological conditions for the alloying with the tungsten carbide of the hot-work alloy steel surface layer and to settle the relationship between the laser alloying parameters, alloyed layer structure and its chemical composition. Before alloying, the degreased specimens were coated with 0.06 and 0.11 mm thick layer of the paste containing the WC tungsten carbide powder with the inorganic binder. Experiments were carried out in an argon atmosphere, at the constant remelting rate (0.5 m/min), changing the laser beam power in the range of 0.7–1.9 kW. The Authors found out that laser melting results in the refinement of structure in the entire laser power range. The different grain sizes were revealed during examinations in the particular zones of the surface layer after laser alloying. The structural and compositional inhomogeneity in the alloyed layer, similar to that noticed by Didenko et al. [55, 56] was also observed. This was attributed to the strong circulation of the liquid metal and rapid solidification after the laser beam has passed, leading to freezing of the structure. It was concluded that the thickness of the alloyed layer is closely connected with the melting parameters and thickness of the fused layer changes significantly along with the laser beam power increase.

The structure and properties examinations of the X40CrMoV5-1 and 32CrMoV12-28 hot work tool steels alloyed with TiC and VC powders with using the high power diode laser (HPDL) was also investigated by Dobrzanski et al. [61]. The surface alloyed layer was obtained by the laser beam remelting of the predeposited layers of TiC or VC (bonded onto the degreased specimens with the sodium glass inorganic binding agent) and investigated steels. The remelted zone (RZ) having the dendritic structure, and the heat affected zone (HAZ) as well as the intermediate zone (IZ) were identified. The observed growth of dendrites occurred from the remelted zone and heat affected zone boundary in the direction of heat removal. The Authors concluded that development of the surface layer by alloying using the high power diode laser with the X40CrMoV5-1 and 32CrMoV12-28 hot – work steels powders improves the service properties (like hardness, abrasion wear resistance, and thermal fatigue resis-

tance) as compared to properties of these steels subjected to the conventional heat treatment only. This means that surface layers fabricated by laser alloying with using the vanadium – and titanium carbide powders, may be used for manufacturing new tools used for hot working.

Lisiecki and Klimpel [62] applied a diode laser for gas nitriding of Ti6Al4V alloy. The aim of the research was production of erosive wear resistant and high hardness surface layers of turbofan engine blades and steam turbine blades made of titanium alloy Ti6Al4V. The laser gas nitriding (LGN) technology was selected to produce titanium nitride precipitates at the surface layers of examined titanium alloys. The Authors studied influence of the laser gas nitriding parameters and partial pressure of nitrogen, as well argon partial pressure in the gas mixture on the surface layers shape, penetration depth, microhardness and erosion wear resistance. For the laser gas nitriding the high power diode laser HPDL was used with a rectangular laser beam of even multimode intensity on the beam spot. Appropriate selection of process parameters permitted to get high quality surface layers with high hardness and erosive wear resistance. The study showed that the erosion resistance of laser nitrided surface layers is significantly higher compared to the base material of titanium alloy Ti6Al4V, and depends strongly on the attack angle of the erodent particles stream. It is expecting that technology of laser gas nitriding can be applied for the increasing erosion wear resistance of surface layers of turbofan engine blades and steam turbine blades made of titanium alloy.

Sieniawski et al. [63] studied the influence of the laser surface treatment of two-phase titanium alloy in order to modify its microstructure and properties. They applied laser hardening and laser alloying on samples without coat and coated by graphite powders in order to form martensitic α' phase, titanium nitrides or titanium carbides as a consequence of the laser pulsed irradiation. It was shown that laser melting followed by rapid quenching cause the formation of the martensitic α' phase, as well as titanium nitrides and titanium oxides in the resolidified zone. Carbonizing by the laser melting of pre-deposited graphite powders on a titanium substrate resulted in a modified surface layer consisting of hard ceramic TiC dendrites spaced in the relatively ductile martensitic matrix. During solidification dendrites grow along the maximum temperature difference direction. The orientation of dendrites within the melt pool is dependent on the stream direction.

Filip [64] studied modification of the surface layer of the Ti6Al4V titanium alloy microstructure and properties by laser remelting in the nitrogen atmosphere, using 1 kW CO₂ laser radiation focused on the sample surface to about 2.0 mm in diameter. The laser remelting process produced a surface layer which consisted of hard ceramics particles of TiN and Ti₂N phases distributed in the martensitic matrix. The hardness of surface layer increased in comparison to untreated alloy due to formation of TiN and Ti₂N particles and depended on the volume fraction of nitrides. The maximum measured value of the hardness (1500 HV 0.2) occurred on the surface of laser treated zone. The wear resistance of laser nitrided layer increased considerably in relation to the base alloy.

Kulka et al. [65–67] studied influence of laser surface modification on the microstructure and properties of conventionally borocarbured 15CrNi6 and 17CrNi6-6 steels and borided 41Cr4 steel. In the paper [65] authors presented the results of laser heat treatment (LHT) of the boride layers produced on the carburized 15CrNi6 low carbon steel. Such a two-step treatment carburizing followed by boriding is termed borocarburing. The laser tracks were arranged by CO₂ laser beam as a single track and as multiple tracks formed in the shape of helical line. The microstructure in both cases consisted of the following zones: iron borides (FeB and Fe₂B) of laser modified morphology, needle-like iron borides, carburized layer with heat affected zone (martensite and alloyed cementite), carburized layer without heat treatment and the substrate (ferrite and pearlite). The improved wear resistance of this layer was found in comparison to borided and borocarbured layers after conventional heat treatment. Such enhancement of wear resistance probably resulted from the presence of globular iron borides in the surface layer after laser surface modification. It was also concluded that the use of laser-modified borocarbured layers may be advantageous under conditions of high abrasive wear of mating parts. In the case of parts, which require high resistance to fatigue, the carburized layer was irreplaceable.

Kulka et al. [66] presented the results of laser surface modification of the borided layers produced on the 17CrNi6-6 and 41Cr4 chromium steels. The laser tracks were melted by CO₂ laser beam as a single track and as multiple tracks formed in the shape of helical line. It was shown that the microstructure in both cases consisted of three following zones: re-melted zone (MZ) (eutectic mixture of borides and martensite), heat-affected zone (HAZ) (martensite) and the substrate (ferrite and pearlite). The XRD scans of the laser modified borided specimen confirmed the presence of the same two types of iron borides (FeB and Fe₂B), like these indicated in the as-borided layer. After re-solidification, in some places with higher iron content, the Fe₃B phase was additionally formed. The surface layer formed after boriding and laser heat treatment (LHT) had a lower microhardness, than that of only borided layer. The wear resistance of laser heat treated was better in comparison to the borided layers after conventional heat treatment.

Paczkowska et. al. [68] investigated CW CO₂ laser boronizing by remelting of nodular iron and predeposited layer (mixture of water glass and amorphous boron). The Authors have selected parameters of laser treatment to achieve different cooling rates for the melting zone. Indeed, different microstructure of melted zones observed for different cooling rates. The polygonal shape of the Fe₂B phase (typical for Fe₂B after laser boronizing) was found in the melted zone cooled at 10³ °C/s. On the other hand, an ultra-fine microstructure was found in the melted zone cooled at the higher rate of 8 × 10³ °C/s. The X-ray diffraction examination revealed higher amounts of hard phases such as Fe₂B and Fe₃C. The microhardness of the melted zone which was cooled at the rate of 8 × 10³ °C/s was about 1300 HV_{0.1}, while for 10³ °C/s the obtained value was below ~1100 HV_{0.1}.

2.4. Laser cladding. Reinforcement of material surface layers is mainly used for increasing their resistance to corrosion, wear, oxidation, and extreme temperatures, as well as the ability to provide lubrication. The use of the surface modification approach to prolong the service life of engineering components that are exposed to an aggressive environment during normal operation has gained increasing acceptance in the recent years [69, 70]. Due to development of different spraying techniques it is now possible to tailor the surface properties of components to provide greater resistance against degradation due to mechanisms such as corrosion, oxidation, wear or failure under an excessive heat load. Furthermore, the surface coating was also cost-effective in the enabling salvage of expensive parts, which were damaged during service. Among the many surface treatment processes that are available today, lasers provide a unique tool for the high quality surface modification. Using the laser-clad process, composite coatings that combine materials exhibiting these properties can be formed. Laser surface cladding (LSC) is capable of producing a wide range of surface alloys and composites of required properties. Application of the laser beam cladding in the surface engineering allows to obtain the porosity and cracking free surface coatings containing uniformly distributed hard particles in the softer and tough matrix [71–75]. Laser cladding is the process whereby a new layer of material is deposited on a substrate by laser fusion of blown powders or pre-placed powder coatings. Multiple layers can be deposited to form the shapes with the complex geometry. This manufacturing process was used for the material surface property modification and for the repair and manufacture of three-dimensional components. The process sequences are shown in Fig. 4.

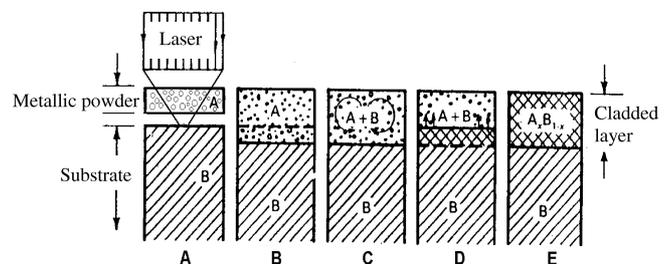


Fig. 4. Schematic steps involved during the laser surface cladding after Refs. [72, 75]

The sample to be processed is moved under the beam in order to produce strips of hard material. The composite powder is transported by an inert gas stream and injected directly onto the moving substrate to the center of the laser beam spot. The laser beam energy is absorbed by the metallic and ceramic powder particles as well as by a thin surface layer of the substrate material at the same time (Fig. 4A). Due to the photon energy absorption, the powder and thin layer of the substrate rapidly reach their melting points. In a fraction of a second, liquid/solid interface moves towards the substrate (Fig. 4B). The depth of the substrate-melted zone depends on the laser power and the interaction time and is kept to a minimum. At this stage, mixing of the molten metallic powder with the substrate and partially dissolved ceramic

Laser modification of the materials surface layer – a review paper

material by a convective fluid flow mechanism takes place (Fig. 4C). When the laser beam moves forward, a resolidification of the molten pool occurs rapidly at a crystallization speed of 10^{-2} m/s [72, 75–78], so the solid/liquid interface moves upwards as shown in Fig. 4D. The uniform composite clad layer is thus produced on the substrate (Fig. 4E) [72, 75]. During the process the material is being fed into the substrate surface under the laser beam by a number of routes including powder blowing, wire feed, pre-placed powder coating etc. Relatively short time of the laser beam cladding powder particles interaction with a liquid matrix permits to preserve the particle shape and size (if carbides, nitrides or oxides of high melting point are used) and does not involve only limited chemical composition and microstructural changes of the metallic matrix which is characteristic when other methods of hardfacing are to be used [71]. The above may be achieved by appropriate selection and control of the processing parameters like: the laser beam power density, the laser beam travel speed, and the laser beam diameter at the workpiece surface [72–75]. Therefore less heat affected zone and less distortion will be caused in the base material by the laser cladding process. In contrast to thermal spraying, laser cladding generates a dense layer, which is fused to the base material. This causes a strong bonding in comparison to the thermal sprayed coatings. Research of the laser cladding covers many scientific issues, including processing techniques, physical and chemical properties of the deposited materials and clad/substrate interfaces, microstructure and phases, rapid solidification phenomena, modeling and simulation, and systems engineering and applications [10]. The laser cladding attracted extensive research over the past 30 years. Up to now, more than 2500 papers have been published in journals and international Confs. In the recent years Polish researchers have also been active in the laser cladding experiments.

Przybylowicz and Kusinski [79] studied the structure and erosive wear of defect free coatings, made of Triballoy T-400 powder, deposited by the laser cladding on iron and nickel based substrates. The Authors showed that the proper selection of the cladding process parameters allowed us to get coatings with low dilution of the base material. Cross-sections of such coatings were examined to reveal their microstructure using optical, scanning electron and transmission electron microscopy, microchemical EDS analysis, phase composition (XRD), hardness and microhardness testing methods. The cladded layer of 1.15 mm average thickness was cracks and porosity free. The structure was not uniform on the coating cross-section with heat-affected zones due to laser track overlapping effect. The microstructure of the cladded track center consisted of a fine lamellar eutectic mixture of Laves and Co based phases forming colonies of 7–15 μ m in diameter, elongated in relation to the microsection. The hardness of laser deposited T-400 coating was high, reaching 63 HRC. The coating showed uniform cross-sectional microhardness distribution, leveling at 800 HV₂ with a drop by 5% in the heat-affected zones. Compared to other deposition techniques the microstructure of the laser coatings showed a high

degree of refinement and chemical homogeneity. The grain coarsening was observed in the heat-affected zones and was explained as being due to the overlapping of subsequent tracks during the coatings deposition. Generally, the laser deposited coatings turned out to be susceptible to extensive erosive wear. This effect was explained by lack of feasibility of the coated material to the plastic deformation during erosion.

Przybylowicz and Kusinski [80] used also laser cladding for the coating of a low carbon steel substrate with WC in Co and Ni-based alloys. The aim of research was to obtain good quality coatings with increased wear resistance. The cladding process was carried out using a CO₂ CW Coherent EFA 51 laser of a nominal power of 1.5 kW. The laser beam of TEM₀₀ mode was focused to a 3 mm diameter spot on the specimen surface. The different laser power and scanning velocity combinations were used during the cladding process. Due to the right selection of the laser processing parameters during laser surface cladding porosity and crack free WC-metal composite coatings were produced. The results of optical and SEM microstructure observations, X-ray phase, and EDS chemical composition analysis as well as cross-sectional microhardness distribution were presented. The longer the laser beam-composite material interaction time was, the higher level of the dissolution of primary carbide phase in metal matrix was obtained. The Authors also showed that the primary WC particles dissolution degree depends also on their mesh size and volume fraction in composite material. The WC/Co hard alloy material coatings were characterized by the highest hardness of 64–66 HRC.

The research groups from Gdansk and Gliwice published several interesting papers [81–85]. Jendrzejewski and Sliwinski [81] modeled temporal and spatial distributions of temperature and strain-stress. The model corresponded to experimental conditions where the multilayer protective coatings were prepared by direct laser cladding of stellite SF6 powder on X10Cr13 chromium steel by means of a 1.2 kW CO₂ laser. For the calculations the effect of base preheating, temperature dependent material properties, and also influence of time-break between cladding of the consecutive layers were taken into account. The calculated temperature fields indicated good bonding of the substrate and coating, which was in agreement with the micro-analytical test results. A decrease of the number of microcracks in the coating with an increase of substrate preheating temperature was concluded from stress calculations and confirmed in the experiment. The best technological results were obtained for the case of single-layer coatings prepared on a preheated substrate. For higher coating thickness required, the processing of consecutive layers with a possibly short time delay is advisable due to effective usage of laser beam energy for preheating and lower temperature gradients. The numerically obtained results indicated that cladding of the single-layer stellite coatings on the preheated chromium steel substrate is preferred. The Authors [81] concluded that for a higher final coating thickness, cladding of the successive layers, with a possibly short time delay between successive tracks, is advisable.

2.5. Laser Ablation. Laser vaporization of materials is well known for many years (it was observed parallel with development of ruby lasers), however, for materials synthesis, known as PLD – *pulsed laser deposition* was applied in 80-thies and is still under expansion for the practical applications [86–90]. During PLD process, the thin film is formed by the laser ablation of a solid target material then its deposition and growth on the substrate.

In the laser ablation process, an intense, with a high frequency, pulsed laser beam is focused on the surface of a target material. As illustrated in Fig. 5, the target material is placed inside a chamber with a controlled atmosphere (vacuum or reactive gas) where is irradiated by a focused, of high fluency, laser beam through an optical window. The vapor plume formed during laser beam/target interaction expands perpendicularly away from the target and condenses on a substrate placed a certain distance from the target. Usually a vacuum chamber is equipped with a rotating target support and a substrate holder, which can be resistively heated up to 900°C. The PLD is a complex physical process in which several phenomena occur. During early stages of the ablation process several subsequent processes: photon energy absorption, rapid heating and melting, vaporization and vapor ionization, plasma emission, plasma heating, as well as detonative plasma expansion, take place due to interaction of the laser beam with the target surface. The ablated material, in the form of some volatile phases, e.g. a gas, plasma or droplets of liquid, is deposited onto the substrate with the well defined structure and orientation. In general, the process can be divided into four main stages:

- interaction of high density laser beam photons with the target,
- dynamic ablation of the target material and generation of highly energetic species (electrons, atoms and ions),
- mass transport from the target to the material in the form of plasma cloud,
- nucleation and growth of thin film on the substrate.

The beginning of ablation occurs above a threshold fluence, which depends on the absorption mechanism, particular material properties, microstructure, morphology, the presence of defects, and parameters such as wavelength and pulse duration (see Fig. 6). The laser's temporal pulse length can have a significant effect on the dynamics of the ablation process. In general, as the pulse length is shortened, energy is more rapidly deposited into the material leading to a more rapid material ejection. With a laser beam of short wavelength (high photon energy) the photo-chemical mechanisms for ablation are active (direct bond-breaking, and explosive disintegration of the material lattice), indeed rather sublimation of material (being in solid state form) than its evaporation from the liquid phase occurs [88–91]. With higher fluence and longer wavelength (lower photon energy) melting, boiling and vaporization take place (frequently explosive boiling happens) [90, 91].

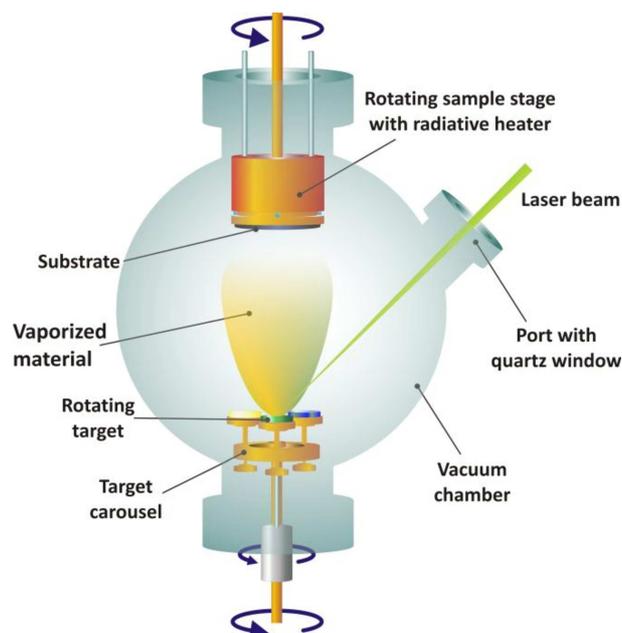


Fig. 5. Typical arrangement of the PLD system

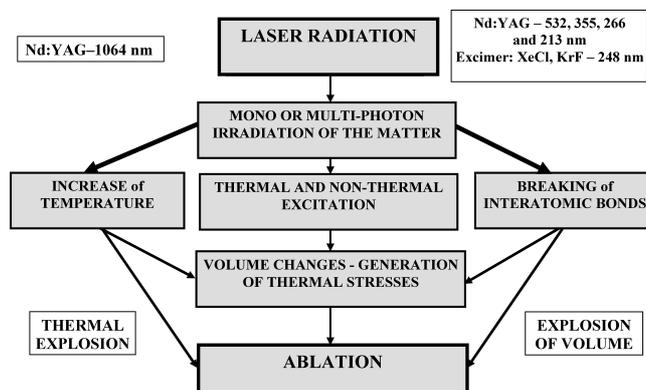


Fig. 6. Illustration of main stages of the ablation process

The thin film grows with velocity reaching of a few dozens of nanometer/pulse. The PLD is probably one of the simplest techniques for thin films manufacture [90–92]. The vapor cloud emitted from the target material during ablation process show many singularities, different from these of vapors formed in other PVD techniques [89–91]. Actually, it is well experienced that the PLD has a unique capability to produce high-quality thin films of various kinds of materials. The technique is also frequently used in elaboration of thin films used as a gas sensors and catalytic devices, multilayer coatings for the tribological and anticorrosive applications, as well as, thin films for biomaterials and microelectronics (thin films of superconductors and piezoelectrics) [92–96].

Kopia [96] used PLD technique for the elaboration of WO_3 thin films. Targets were initially prepared by compacting powders of WO_3 under a pressure of 140 MPa during 5 min. Then the pellets were sintered at $T = 1200^\circ\text{C}$ for 2 hours. The WO_3 thin films were deposited on [100] oriented Si substrates, using the Neocera ablation system equipped with Q-switched Nd-YAG laser Continuum Powerlite DLS (maximum energy 2J, $\lambda = 266$ nm, pulsed duration $\tau = 8$ ns).

The characteristics of the deposition system were: a target-substrate distance of 70 mm, the oxygen pressure in the deposition chamber was $P = 5$ Pa. The deposition conditions were the following: a frequency of $f = 10$ Hz, energy density at the target, $\varepsilon = 7, 8$ J/cm², substrate temperature, $T = 25$ or 650°C , deposition time, $t = 30$ min. After PLD deposition thin films were annealed at 450°C for 12 h for homogenisation in vacuum and then coated with Au or Pt by means of sputtering. The crystallinity of the WO₃ thin films was examined by means of the XRD (PANanalytical EMPYREAN DY 1061) and Cu K α radiation in grazing geometry $\alpha = 1^\circ$. The surface morphology of the films was examined using atomic force microscopy (AFM – Veeco DIMENSION ICON-PT). The thin film microstructure was observed by means of transmission electron microscopy (TEM – JEOL JEM CX200). The electrical resistance (R) of the WO₃ thin films in air, CO and NO₂ atmosphere, was measured using the two points resistance method. The aim of research was production of thin films, by means of laser ablation technique, that would be sensitive to presence of certain gases. The examination showed that the substrate temperature has strong influence on the structure of the deposited thin films. The structure of WO₃ thin films was monoclinic when substrate temperature was equal to 25°C , while the tetragonal structure was revealed in the thin films deposited at 650°C . It was shown [96] that the electrical resistance in the thin film increases at the moment of introducing NO₂ into the atmosphere and drops down at the moment of introducing CO atmosphere. The reaction time was less than several seconds. When NO₂ or CO inflow is cut off and the chamber is blown through with the air, the resistance returned to the value observed before the analysis, which shows that the thin film surface was regenerated. The stronger signals for both gases were obtained at higher temperature $T = 300^\circ\text{C}$. Indeed, it was proved that using PLD technique it is possible to get a good quality WO₃ thin film, which can be used as a gas sensor for both CO and NO₂ gases.

Radziszewska [97, 98] studied the structure and chemical composition of $\{\beta\text{-Al-Mg}\}$ mono- and Al-Mg/Ni multi-layer thin films deposited by means of PLD technique operating at the following conditions (IV-th harmonics ($\lambda = 266$ nm) radiation of Q-switched Nd:YAG laser operating with the fluence of 2.3 J/cm², and substrate temperature 200°C). The Al-Mg and Ni alloys have attracted wide interest due to their low weight, good corrosion resistance and thermoelectric properties. The multilayer of Al-Mg-Ni was obtained by the subsequent ablation of two targets: $\beta\text{-Al}_3\text{Mg}_2$ and Ni (99,999 %) and vapor deposition onto the MgO (001) substrate. The ablation process was initiated from Al-Mg target and then carried out with Ni target, and so on. Cross-sections of multi-layer thin films were examined by means of the TEM. The thicknesses of Al-Mg-Ni typical multi-layer, was about 154 nm (whereas, the thickness of particular layers, starting from the MgO substrate, of about: 30, 20, 45, 10, 45 and 35 nm. The electron diffraction analysis indicated the presence of nanocrystalline Al₆₅Mg₃₅ and Ni layers in multilayer film, both phases having FCC structure.

S. Kac and M. Kac [99] investigated of Al-Cu-Fe thin films obtained by PLD technique. They applied Nd:YAG pulsed laser with wavelength of 355 nm and with laser fluence ranging from 8 J/cm² to 10 J/cm². The metallic Al₆₅Cu₂₃Fe₁₂ alloy targets were used for the ablation. Using PLD technique the Authors were able to obtain homogenous thin films of thickness ranging from 260 nm to 550 nm (depending of applied laser fluence) free of porosity and cracks. The Authors concluded that the laser fluence and the substrate temperature, during deposition of Al-Cu-Fe thin films by PLD process, influence strongly the chemical composition and morphology of obtained films.

Major et al. [100, 101] used the hybrid PLD system (Pulsed Laser Deposition + magnetron sputtering), equipped with high purity titanium (99.9% at. Ti) and carbon targets, for multilayer TiN/Ti/a-C:H coatings deposition. The aim of research was to enhance the cracking resistance properties of coatings by reduction of cracks propagation. The metallic Ti buffer layer was deposited as a first layer on the substrate, to increase the adhesion properties of the coating. The detailed TEM/EDS examination showed the presence of carbon layers placed in a sequence with TiN ones. Moreover, EDS line-scan analysis confirmed the presence of very thin metallic Ti layers at each a-C:H/TiN interfaces. It was also shown that as deposited coatings were characterized by crystalline/amorphous multilayer structure. The TiN layers revealed columnar microstructure and high defects densities (dislocations). The carbon layers were amorphous. Furthermore, after detailed TEM studies of the deformed multilayers, the authors [100, 101] demonstrated that TiN ceramic layers, as well as a-C:H layers, brittle cracked while very thin metallic layers prior to cracking were plastically deformed. It was proved, that the presence of metallic phase lead to deviation of direction of small cracks resulting in overall coating cracks resistance. In a consequence, the TiN/Ti/a-C:H multilayer coatings, due to their relatively low friction coefficient and good biological inertness, might be applied for pump parts supporting artificial heart systems.

Mroz et al. [102] used a KrF laser ($\lambda = 248$ nm, $\tau \sim 20$ ns, fluence – in the range $2\text{--}12$ J/cm²) for the deposition of intermetallic coatings produced by ablation of the FeAl and Ni₃Al alloy targets. After deposition fine-grained microstructure of thickness in the range from 50 to 1000 nm was formed in the deposited films. The thickness of deposited layers was dependent on substrate temperature and ion energy. Basing on diffractometry measurements the Authors showed that at high laser energy fluence in the case of the FeAl target, the matrix comprises the polycrystalline Fe₃Al intermetallic phase, while at low fluence the matrix comprises a solid solution of aluminum in iron (amorphous phase). In the case of the Ni₃Al target, the matrix comprises the polycrystalline Ni₅Al₃ orthorhombic and Ni₃Al₄ cubic phases.

There are also other research teams in Poland that used the laser ablation for production of thin films; however this review is limited to the papers presented during STL Confs.

2.6. Laser cleaning. Lasers are now used on a regular basis in the restoration of stone surfaces of individual monuments and the architectural surfaces of buildings of great historic and artistic value, as well for the surface cleaning and renovation of historical paper documents [103–110]. The laser cleaning systems contributed to the increasing applications of lasers in conservation, particularly during recent ten to fifteen years [111]. The laser cleaning technique utilizes intense laser radiation to selectively contaminants removal from a solid surface while leaving the underlying substrate largely unaffected [109–111]. The technique exploits differences in the optical and thermal properties of the underlying substrate and the contaminant layer as well as the ability of precise control material heating depths and removal rates by controlling laser beam parameters such as pulse time (or scan rate), wavelength, and fluence (or intensity). The laser cleaning is thought to be a cost effective way, alternative to commonly used methods of surface cleaning in conservation of art works like: water jet, abrasive blasting, or chemical based cleaning methods. The typical industrial applications of laser cleaning include oxide and coating removal, tool cleaning, removal of grease and paint, as well as adhesion promoting pre-treatments for welding, gluing, and painting [104–116]. The laser cleaning can also be used for efficient removal of very small particles from delicate substrates such as silicon wafers and photolithographic masks [110–114]. The application of laser technique gives possibility of almost full control of the encrustation removal process at the surface of art works. An example the analysis of color of cleaned sandstone and limestone before, in the course of and after cleaning with the impulse laser radiation (the pilaster in the lantern in the Sigmund's Chapel and the little angel figurine on the throne wall in the Batory's Chapel in Wawel, Cracow was presented by Marczak and Koss [106]. The selective and precise interaction of the light beam is a fundamental advantage of non-invasive treatment of more or less tightly connected unwanted surface layers. Even if the last generation of laser systems improved the understanding of their effects and their engineering, laser cleaning is not yet a mature and routine technology for earlier restoration tests. There is still lack of in-depth knowledge of the basic laser-artwork interaction mechanisms. Indeed, there are conducted research projects concerned on understanding of laser-matter interactions.

Marczak et al. [108] presented set of equations describing in one-dimensional (1D) model phenomena accompanying to laser-matter interaction. The target geometry includes two and four layers of different materials, irradiated by ns laser pulses. The effects of radiation absorption and transport, heat conductivity, target transit to plastic state, melting and evaporation are taken into consideration. The Authors described one-dimensional (1D) numerical model developed especially for the process of removal of top materials layers (ablation process) in the range of low power densities of laser radiation (from 10^6 W/cm² to 10^9 W/cm²) and nano-second laser pulses, which are commonly used in the cleaning of art works: encrustation removal. The selected results of numerical calculations were also shown and discussed. It was concluded that

the developed physical model and computer codes show high versatility as well as correctly present qualitatively, quantitatively behavior of illuminated objects. Based on the numeric approach, the influence of the impulse laser beam parameters, like: energy density (power) of the laser radiation, the time of duration of a laser impulse and the number of impulses, on the rate and efficiency of the ablation process of foreign accumulations was determined. The results can be utilized for a description of interaction of one or more laser pulses in any period of time and in a wide range of laser power densities, utilized during cleaning of artworks. The extreme care should be taken for the optimization of the operational parameters in order to ensure the absence of any negative effects induced on the artwork. In fact, numerical multi-layer model describing interaction of laser beam radiation, as well experimental verification was delivered [108]. The developed numerical model describes also well interaction of low power density (10^6 W/cm²) laser pulse with multi-layer metallic sample. The irradiation of multi-layer sample, containing three metal components (Cr-Cu-Al) deposited on quartz substrate, by means of laser pulse heating, allowed melting and interdiffusion between two internal Cu and Al layers. Top Cr layer remained in solid state. This result documented theoretically and in the experiment allows extracting a basic conclusion important in a laser cleaning of multi-layer metallic cultural heritage objects: how possible and probable can be their physical modification and chemical reciprocal modifications in the case of different melting points of metals. For higher power densities in the range 10^8 W/cm²– 10^9 W/cm², laser radiation pulse generates strong pressure wave inside the sample. The pulse of tensile stresses undergoes transformation into the pulse of compressive stresses after reflection from back free surface. Such dynamic changes of stresses can cause damages of objects with thin walls. The use of lasers for the surface cleaning and renovation of historical paper documents requires a careful selection of interaction parameters according to the chemical composition of the paper material and the surface contamination as well [115].

2.7. Laser Shock Processing. Laser shock processing (LSP) is a relatively new and promising surface treatment technology for strengthening, roughening, as well as cleaning the surface layer of materials [116–118]. The potential applications are directed to aerospace and automotive industries [119]. The LSP uses a high-energy pulsed laser to irradiate a metallic surface for very short time (a few nanoseconds). Once the metal surface is irradiated by the high energy laser pulse, the surface of the material is heated, vaporized and forms a plasma. As this plasma expands, an intense shock wave propagates into the metal. Shock waves can produce one or the combination of the following metallurgical effects: generation of point defects, dislocations and twins, phase transformations and precipitation [120, 121]. Due to absorption of the laser beam energy, the thin surface layer of the treated material, especially for alloys of a low melting point such aluminum is melted. In order to avoid this melting, the metal surface is covered by a black paint (absorbing layer, Fig. 7a). Next, a

thin layer of water (transparent layer, Fig. 7a) is applied on top of a treated sample, which confines expansion of the plasma and enhances the effectiveness of the process [122, 123]. When the laser beam is directed onto the surface to be treated, it passes through the transparent coating and strikes the opaque overlay. It immediately vaporizes a thin surface layer of the overlay. The vaporization of the black paint produces rapidly expanding plasma that is confined against the surface of the material by a constraining layer of water (see Fig. 7b). The plasma causes a shock wave by its expansion and leads to the plastic deformation of the material. Water decreases the expansion of plasma in the surrounding atmosphere and produces up to ten times higher pressure on the material surface. The pressure propagating into the treated material as a shock wave can induce microstructural changes, cause a high increase of dislocation density, influence the surface roughness of the material as well as produce high residual surface compressive stresses [122–125]. If the surface is insulated from the increasing temperature by a protective absorbing layer, the laser treatment becomes purely mechanical. When the shock wave generation occurs together with surface ablation and melting, the treatment becomes thermo-mechanical [123]. Rozmus-Gornikowska et al. [124] examined the effect of the laser shock processing on microstructure, mechanical properties, residual stress level and roughness of the surface layer of a Ti6Al4V titanium alloy. The sample surfaces for the laser processing were prepared using the standard metallographic procedure of grinding and polishing. Then, before the LSP, polished sample surfaces were coated with a laser energy absorbing layer (the 50 μm thick black paint) and immersed in water (about 3 mm beneath water level). The laser system used in this study was a Q-switched high energy-pulsed Nd:YAG laser with a wavelength of 1064 nm, pulse duration of 18 ns and power density used was 10^{12} W/m² and 10^{13} W/m².

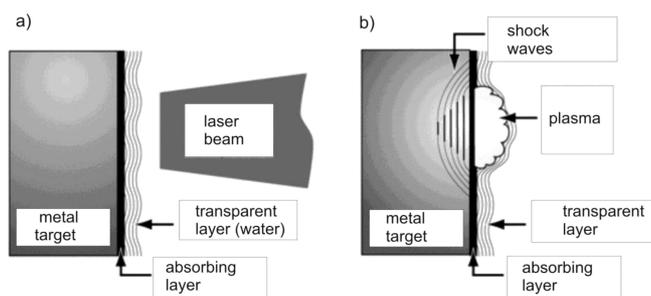


Fig. 7. Schematic representation of the laser shock processing (a) metal target with absorbing and water overlays (b) shock wave generation by laser beam after Ref. [124]

The process was performed in an air atmosphere. Before laser processing, the Ti6Al4V alloy samples showed a homogeneous microstructure with very fine grains of α and β phases. After laser treatment in the central part of the treated area cracks were visible, while the periphery part was strongly folded. During the LSP, the surface of the treated area was partially melted and then rapidly solidified. When 5 subsequent laser shots were injected to the same area the resolidified layer was not uniform and some pores at the boundary

with un-melted substrate were present. In both cases, certain structural refinement was observed in the surface layer, the zone lying just beneath the melted layer. The TEM investigations revealed formation of the surface layer composed of three zones (sub layers): external – resolidified and partially oxidized, central – martensitic, and internal – deformed, with high dislocation density level. Due to the Gaussian energy distribution in the laser beam, the melted layer depth in the center of the treated area was thicker than in the periphery part. Since the laser processing of the samples was conducted under water in an ambient atmosphere, oxidation may occur (all main alloy elements (Ti, Al and V) show a high affinity to oxygen). For both effects, the presence of surface oxides and tensile stress in the resolidified surface layer were responsible for the cracks in the central part of the laser processed areas. The shock waves spreading during the LSP from the center to the treated area periphery involved folding of the thin melted layer. Indeed, after rapid solidification the resolidified surface remained folded. The measurements of the surface roughness showed that for all the investigated samples Nd:YAG laser treatment provided an increase in the surface roughness. Ra (arithmetic average of the absolute values of all the points of the profile) increasing from 0.1 μm (before treatment) to: 0.8 μm for both treatments with 10 TW/m² and 1 TW/m² power densities. The increase of the surface roughness was attributed to both material ablation and melting. The nanohardness values measured on the polished cross-sections showed that the hardness of the layer contained martensite and a high density of dislocations (approximately up to 0.5 mm) which was much higher (varied between 360 – 480 nHV) than that of the matrix (290 nHV). Also the Young's modulus values of the investigated internal deformed surface layer (140 GPa) was slightly higher than that of the matrix (127 GPa)- as reference see [124, 126].

3. Other laser surface techniques

3.1. Laser remelting of multilayer coatings. In many systems is difficult to get multicomponent intermetallic samples using traditional casting. One possible technique is annealing of multilayer coatings (composed of subsequent layers of different elements – intermetallic components), deposited by means of PVD techniques. The interdiffusion, which is necessary for coating homogenization, is a long term annealing. An alternative, much faster process, is the laser remelting of multilayer coatings [127]. The samples were prepared using a classical vacuum deposition of thin metallic layers. Average thicknesses of metal layers, determined by the scanning transmission electron microscopy were: Cr: 40 nm, Cu: 250 nm, Al: 100 nm. A laser pulse irradiation of multi-layer sample, containing three metal components (Cr/Cu/Al) deposited at a quartz substrate allowed melting and diffusion of two internal Cu and Al thin films. The top Cr layer remained in solid state.

3.2. Laser texturing. In many practical applications the surface roughness is an important parameter and in many cases

modification of surface topography is necessary. The laser texturing is a recently well developed technique, aimed at achieving optimum craters shape on surfaces of rolls, engines (pistons and crankshafts – to reduce friction-related energy losses in engines and drive systems), drive systems and other devices based on metals (steel rolls, prosthesis made of Ti alloys for improved biological adhesion), ceramics (silicon solar cells), and composites. In the texturing operation, a high energy and high repetition rate pulsed laser beam is focused on the moving surface of a rotating or moving elements, creating a localized melted micro-pool on the surface. These geometries range in size from 5 to 200 microns and include hemispheres, squares, lines, and divots.

Burakowski et al. [128, 129] investigated the ablative laser texturing of the crankshaft pin of internal combustion engine, made of 41Cr4 steel. The aim of research was formation, by means of laser ablation process texture cavities, in shape of the spherical or rectangular cavities that could work as micro containers for the lubricant. The Authors expected that experimental tests should verify the advantage of surface texturing in reduction of friction and better durability of engine crankshafts.

Dobrzanski and Drygala [130] used Nd:YAG laser radiation for texturing of multicrystalline silicon used for the solar cells. The aim of the study was the increase of incident solar radiation absorption by the laser texturing of cell surface. The Authors demonstrated that laser surface treatment introduced the defects into the top layer of processed material that deteriorated the performance of the solar cells. To reduce this effect they applied post-laser texturing etching, which permitted to remove the distorted layer and improve efficiency of the corresponding solar cells. It was concluded that laser texturing of multicrystalline silicon together with the post-texturing chemical etching may be successfully used in the production of high-tech multicrystalline silicon solar cells.

Antoszewski [131] studied formation of textured sliding surface of SiC rings by means of laser micromachining. The cavities were generated with Nd:YAG pulsed laser (with third harmonic frequency – wavelength of 355 nm). The aim of the research was the improvement of the tribological properties of the treated material (SiC rings). It was shown that surface modeling involved production of blind dimples in the shape of a cylinder or, more frequently, a truncated cone. On the basis of the friction experiments the Author concluded that the positive effect of texturing was more visible for the larger diameters of cavities (cavity diameters should be in the range of 138–150 μm) and larger degree of blackening (the preferable degree of blackening is 42–50%).

The laser textured roll surfaces are becoming increasingly popular in the manufacturing and processing of steel sheets. In the laser texturing, a high energy laser is used to rapid melting of a small area of the rolls surface. As a consequence, the surface tension should cause the pool to deform [127]. Du et al. [132] showed that the laser texturing process increases the rolls surface hardness. The surface hardness of the bumps is much higher than that of the untreated areas of the roll. Moreover, the surface tissue of high hardness is able to improve

the abrasion resistant quality of the roll surface and extends the service life of the roll.

4. Concluding remarks

The state of the art of laser processing in surface materials modification in Poland, based on own experience, coworkers and coauthors results, as well literature review has been reported. The research data available in the literature in the past 50 years has demonstrated numerous applications of lasers in the surface materials processing over the world, including Poland. Especially, the availability of high power, CO₂, Nd:YAG (with fiber optic beam delivery), diode and fiber lasers created the revolution in the area of laser-materials processing. These lasers provide illimitable possibilities of their use in the surface processing. The curriculum concerning the historical development of lasers and laser technology in Poland, laser-matter interaction, as well basis of different laser techniques applied in the materials surface engineering (solid state hardening, melting, alloying, cladding, ablation, shot peening, cleaning and texturing) were reviewed, and compared with results of collaborators, as well as with a wide range of Polish researchers. The examples presented in this paper are selective and in many cases relation with first the author research is easy to recognize! It could be concluded that overall state of research on laser application in the surface engineering in Poland is well developed and still growing industrial application is observed.

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