ABLATIVE LASER CLEANING OF MATERIALS

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Abstract

On the base of literature data as well as authors' works a review of the state-of-the-art in ablative laser cleaning of surface layers of various constructional materials with encrustation produced in physical and technological processes is presented in the paper. The process and mechanisms occurring in the ablative laser cleaning are described. Three types of the most frequently used lasers offer characteristic advantages understood as average power, pulse operation, wavelength, optical feedback with material processed, and fiber delivery. The process of surface layer cleaning of materials and machine elements can be carried out in various ways. In general, when using pulse laser radiation, five different mechanisms of removal of particles, encrustations, or coatings can be applied. So, the process of removal can be performed via following physical processes: surface vibrations, particles oscillations, thermal expansion of particles (or encrustation), generation of so called detonation wave over surface being cleaned, and laser ablation. Lasers are especially useful for removal of layers from many types of substrates like wood, metals, plastics, composites, stones, ceramics, leather, and others. The important advantage of laser cleaning and surface modification is the capability of processing automation which is related to process repeatability, ease of parameters controlling, possibility of strengthening in zones difficult to access, high precision of interaction and high efficiency as well.

Keywords: *laser ablation, cleaning of materials, surface layer*

1. Introduction

A concept of the use of laser radiation for selective removal from the surface an optically absorbing different substance, for instance a secondary encrustation, is well known for years. It was first demonstrated in 1965 by Arthur Schawlow, one of the laser inventors, who evaporated selectively absorbing black pigments of printing ink from a strongly reflecting white sheet of paper [14].

In the seventies, during laser-matter interactions, a phenomenon now called a laser ablation, was observed and reported [1-7, 13, and 14]. Traditional cleaning methods using, for example, water under high pressure with addition of various abrasives or chemical compresses joined with brush cleaning, remove encrustations mechanically. Competitive methods frequently used in production processes apply chemical methods for pollution removal (for instance etching) or ultrasonic techniques.

In order to perform precise cleaning of small areas of museum objects or artworks, electronic and machine elements made of various structural materials one should use laser radiation which in some cases is the only effective cleaning method.

2. Laser ablation

This term can be understood as an evaporation of surface layer of various materials: metals, ceramics, polymers and composites. Ablation occurs during laser pulse duration and in this process absorption and scattering of laser radiation by material is accompanied with breakout of a material (in a form of vapour, liquid, or particulates). In result of material surface irradiation by laser pulse of an appropriate power density such phenomena as radiation absorption and thermal or photochemical processes are observed.

A small radiation reflectivity is desired and a properly high excitation of material surface needs high intensity laser beams and a low absorption depth of laser radiation.

In ablation process a few stages can be distinguished:

- energy deposited in a volume reaches ablation threshold value;
- evaporation of material surface layer can be generated either in a thermal (pyrolithic) process or in a photolithic way (for ultraviolet radiation);
- plasma plume consists of particle fragments of the material, electrons, ions and reaction products;
- plasma plume generates absorption and scattering of incident laser radiation pulse;
- generated acoustic wave (moving into material interior) can increase reaction products efficiency after reflection from phase boundary.

A thickness of evaporated surface layer (ablation depth) depends on:

- material parameters: *optical* – absorption depth of laser radiation; *thermal* – thermal conductivity, temperature diffusivity, and heat of evaporation;
- laser beam parameters: laser wavelength (a strong dependence of material absorption coefficient on laser wavelength), energy density, laser pulse duration.

For particular applications the following parameters of a material surface layer should be known:

- **material**: thermal conductivity, specific heat, elastic constant, yield point, coefficient of thermal expansion, pressure, dependence of melting point, coefficients for laser radiation absorption and reflection, and many others;
- **laser**: laser radiation wavelength, power (in the pulse or averaged one related to repetition rate), laser beam divergence, pulse duration, lateral energy density distribution in the beam;
- **irradiation geometry** for processed material (size of laser spot);
- **processing method** and **ambient medium**: neutral gas atmosphere (for instance helium), reactive gas atmosphere (for example nitrogen at specified pressure), or vacuum.

3. Point of laser surface cleaning

In a process of particles rejection by photons, so called photo-rejection, three essentials forces responsible for particles attachment to the surface are taken into account. These are: *van der Waals* force, capillary force (caused by particle forces), and electrostatic force. When a distance of molecules decreases rapidly increasing repulsive forces appear while the distance rises a bit – adhesive forces attaching particles to the substrate are observed. To overcome relatively large adhesive forces attracting particles to the surface without surface damage a laser cleaning using photomechanical reactions can be applied [1-11].

In result of efficient laser radiation absorption in surface layer (oxides, corrosion, patina, fats, oils, paints, varnishes) a significant and rapid temperature rise is observed. Next plasma is generated from which, due to convection and electron thermal conductivity, energy is transported inside the material where laser radiation can not reach. A special boundary is created, called ablation front, in which high gradients of plasma density and temperature exist. Ablation front separates two zones in which material motions are opposite. From the zone closer to the outer surface a "runaway" of heated material occurs in the direction perpendicular to heated surface. In the other zone a motion of matter is directed inside the substrate as a narrow zone of weakly heated matter condensed by shock wave.

The shock wave propagates according to momentum conservation law as a reaction of a system to rapid evaporation of surface material. If a contaminating layer is very thin, then the shock wave after reflection from the substrate surface (of inter phase boundary) changes its direction of propagation and multiplies the effect of rejection of contaminating particles. For the thick layer being removed a shock wave converts to an acoustic wave which leads to strong vibrations of a solid substrate in the irradiated area thus multiplying efficiency of cleaning effects.

a) b)

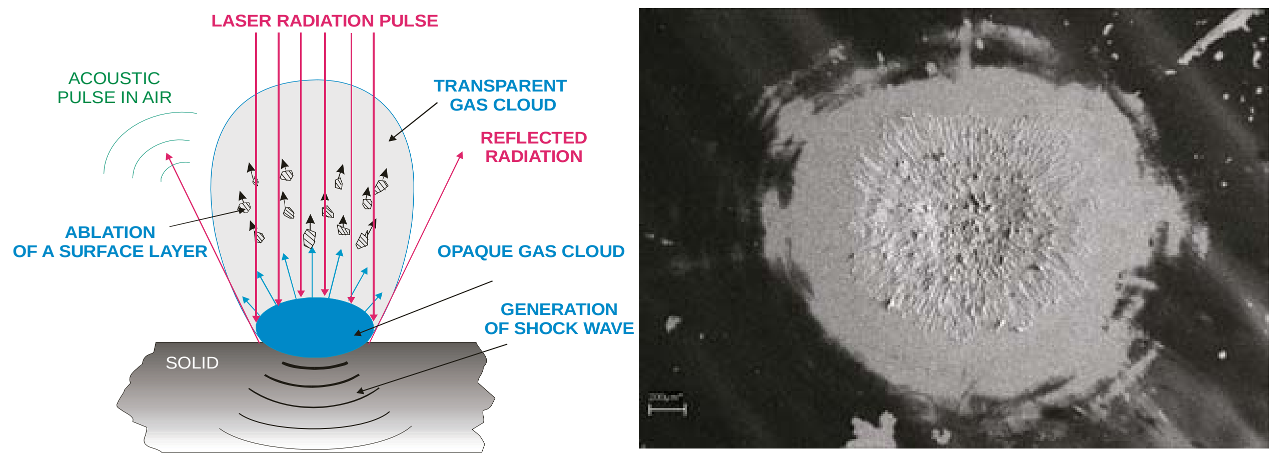


Fig. 1. Interaction of a pulse laser radiation with matter for a certain time "t" and after laser pulse termination: a) for power density $q \approx 10^8$ - 10^9 W/cm^2, b) final effects of shock strengthening (laser shock peening – LSP) – variant for scheme a) for aluminum PA31 alloy loaded by two laser pulses (b) - $q \approx 0{,}33 \cdot 10^9$ W/cm^2

After removal of encrustated layer, the original surface is automatically protected against consecutive damages because phase boundary does not more exist – the shock wave does not reflect any more but is absorbed by the substrate. Ablation front depth depends primarily on laser wavelength and amounts to 0.3-1 μm. This means that we are able to control removing layer by layer, provided special selection of laser radiation parameters. Moreover, we can control laser beam parameters continuously (pulse duration, peak power density, and pulse repetition rate). Delivered power should be sufficiently high so that immediate large heat flow from particle to particle, necessary for explosive rejection of particles from he substrate would be possible, and simultaneously – low enough to not exceed a damage threshold for substrate surface. Surface cleaning by removal of particles attached to it or any encrustations can be performed in dry or wet processes.

3.1. Dry cleaning

Two extreme cases can be distinguished for dry cleaning. In the first case a wavelength strongly absorbed by substrate only is selected (Fig. 2a). In the next one laser radiation is efficiently absorbed only by molecule polluted of surface (Fig. 2a).

In the first situation a process of particle detachment is explained by a rapid growth of substrate thickness caused by its heat expansion resulted from absorption of laser radiation (a change of centre of inertia). Despite the fact that this growth of substrate thickness can be very small, below 1 μm, it proceeds so rapidly that corresponding acceleration can reach 10^7g values (Fig. 2a).

This huge acceleration causing particles removal from the surface can be also achieved via strong absorption of radiation by the particle alone.

3.2. Wet cleaning

Laser clearing can be also efficient when a thin liquid layer is distributed on a soiled surface right before laser pulse incidence. In particular, a thin water layer or water solutions of organic or inorganic liquids can be applied. Rapid ablation of a liquid layer creates giant pulse forces which overcome adhesive forces at the particle-substrate border and detach particles.

Ablation of a thin liquid layer can be caused by selective heating by laser radiation, for example heating a substrate only, heating a thin liquid layer only, and or mixed heating of particle and a liquid layer together. One of these solutions is illustrated in Fig.3. This method was developed and improved because of its best efficiency of laser cleaning of various soiled substrates.

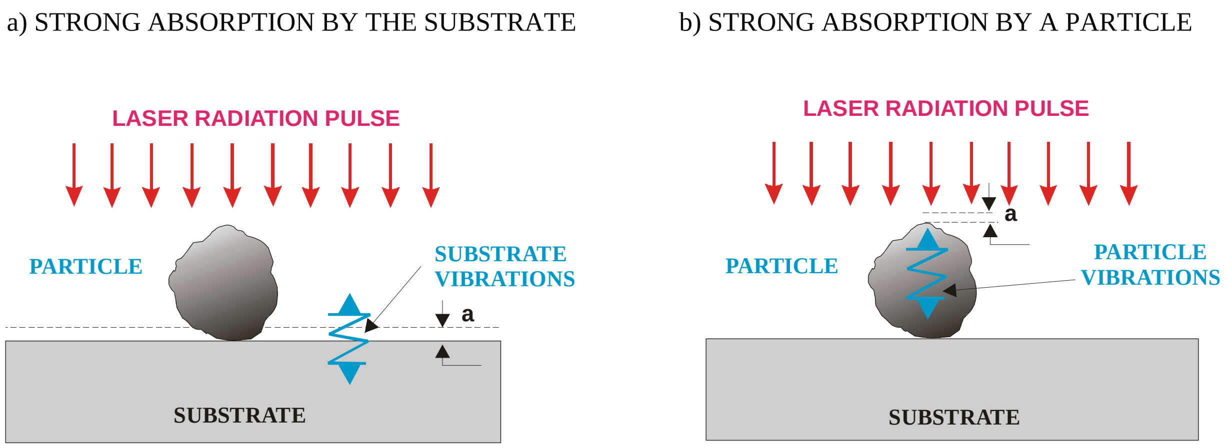


Fig. 2. An illustration of extreme cases for „dry" removal of microparticles from substrates

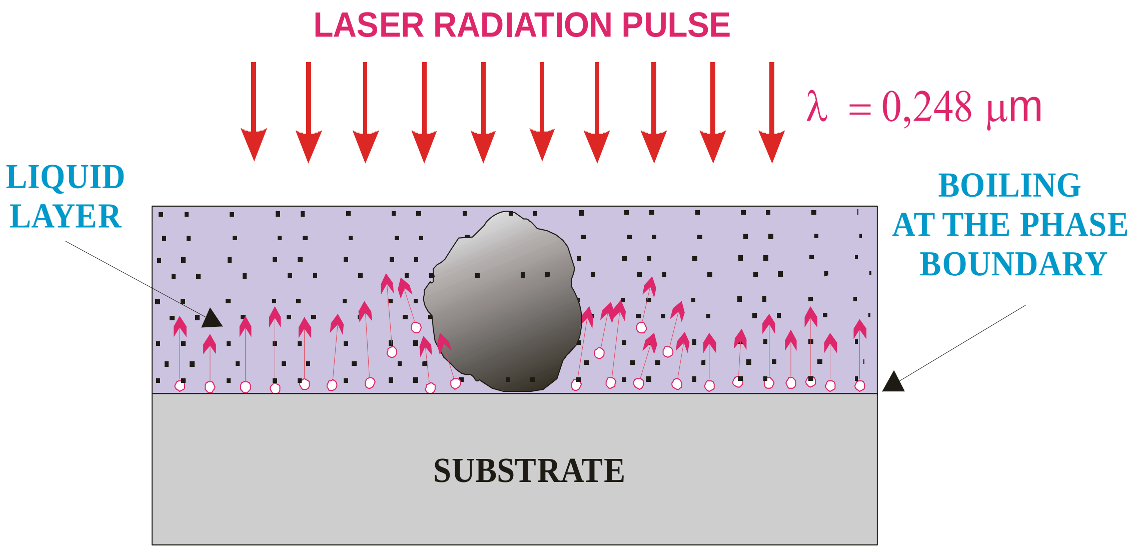


Fig. 3. An illustration of extreme cases for „wet" laser surface cleaning – strong absorption by the substrate

3.3. Shock wave removal of particles

In nanotechnologies and electronics of large integration scale there are applied shock waves generated closely above the cleaned surface in ambient gas (argon, nitrogen). In the vicinity of substrate surface, laser radiation is focused so as not to exceed 10^{11} W/cm^2 power density. In a lens focus heating and ionization of gas occur and high temperature dense plasma is generated, shortly called a laser spark. Expanding plasma generates a shock wave on the front of which a high pressure jump blows out microparticles from the surface [1, 10-12].

Our measurements devoted to visualization and detection of a shock wave motion in air (laser spark expansion) using stroboscopic differential camera showed more than 10^8 locations of a shock wave front per second [5]. Using this camera and 25-30 ps in duration, 8 ns distant diagnostic laser pulses, plasma expansion velocity was measured. Estimated shock wave speed in air amounted to over 10^7 cm/s [7].

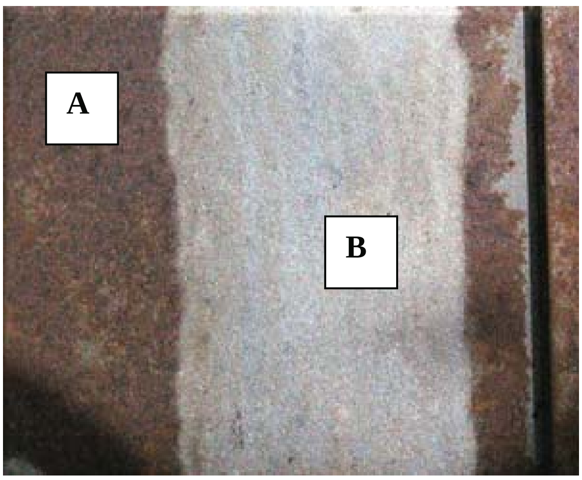
4. Surface cleaning

Different materials, like: steel, cast iron, aluminium and copper alloys have been subjected to cleaning from impurities of oxide coats, chemical deposits, paints, tarnishes with application of the ablation method. A pulsed type ReNOVA Nd-YAG laser with Q-switch modulation and frequency conversion emitting radiation of wavelengths: 532nm; 355nm; 266nm as well as a pulsed laser TEA CO_2 working on the basic wavelengths 1064nm were used in experiments. Test pieces of different materials with impurities in form of coats; like patina on copper, corrosion on brass, dirt and fat on cast iron or technological coats, namely, lacquer on transformer plate, electrolytic coatings, technological deposits after bath nitriding were subjected to the laser cleaning. Several variants of laser treatment, using a TEA CO_2 laser, comprising different laser power densities and pulse number were under examination.

Selected results of the mentioned above investigation are presented in the paper. A modern set of a stereoscope microscopy with digital recording was used in examinations of surfaces subjected to the cleaning process. A scanning electron microscopy (SEM) and X-ray micro analysis was subjected to study of chemical constitution appearing on the surface before and after the laser cleaning.

Results of the laser cleaning of the steel sheet surface, covered formerly with corrosion products are presented in Fig.4, left and right; surface before cleaning with corrosion products zone A and zone B the area after the cleaning. A good quality of surface, like metallic one was observed after the cleaning process. Areas with intensive corrosion destroy were subjected to the process repeatedly. In order to intensify the cleaning, an Nd: YAG laser can also be used (Fig. 4 right). This laser can be used to clean: corroded, fated, dusted as well as covered with organic compounds surface layer of grey cast iron (Fig.5). As a result of concentration of the laser beam of energy density of order 4 J/cm^2 on the small area, the surface of a high cleanness, free of impurities, fats and oxides is obtained. Graphite concentration in the cast iron improved laser absorption leading to the process efficiency.

a)



b)

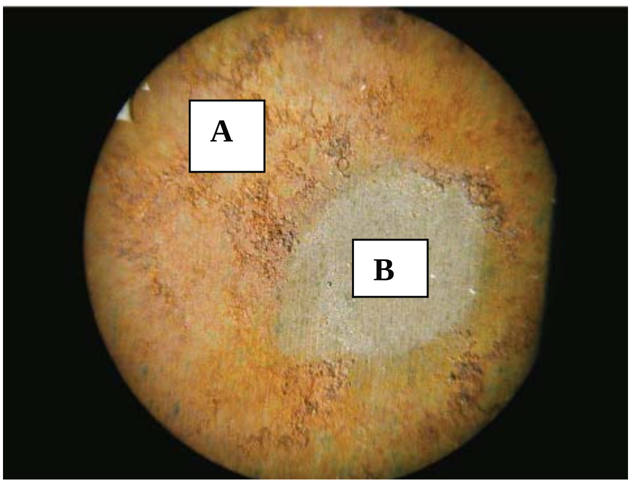


Fig. 4. Surface of constructional steel sheet of ordinary quality formerly covered with corrosion products and subsequently cleaned using laser beam; left picture - TEA CO_2 laser with energy density of laser beam of 9 J/cm^2, pulse duration 150 ns; right picture – Nd: YAG laser with energy density of laser beam of 5 J/cm^2 , pulse duration 10 ns; A – area cover with corrosion products, B – area after laser cleaning

a) b)

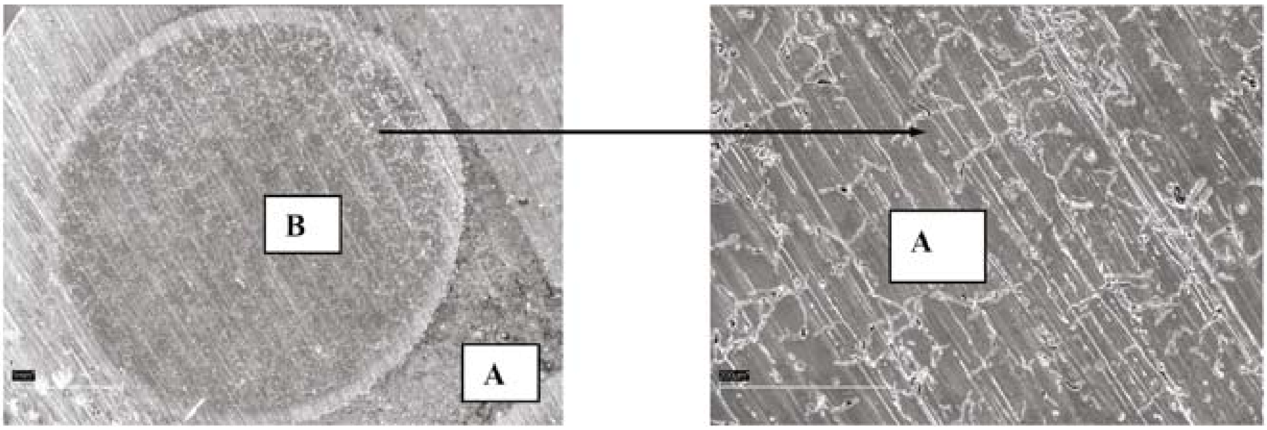


Fig. 5. Surface of low alloyed grey cast iron subjected to laser cleaning using Nd: YAG laser with energy density of laser beam of 4 J/cm^2, pulse duration 10 ns (one pulse); left picture – general view of laser cleaned surface, right picture – surface morphology after cleaning; A – area before cleaning, B – area after laser cleaning

Laser cleaning of aluminium and its alloys from organic and non-organic impurities as well as oxides seems to be very perspective in comparison to a vapour or sand blasting which cause increase of surface roughness and penetration of an abrasive medium into the surface of cleaned materials. Application of the Nd: YAG laser gives possibility to control and repetition of process. In respect to the applied parameters, like: energy density, pulse duration, the process could be performed at low energy density without defecting of the substrate or at high energy density leading to surface development. Multiplication of the process in a controlled way causes cleaning to a high degree; impurities are evaporated as well as oxides are degraded. Effects of a local surface hardening could also be observed.

Thanks cleaning joined with the surface development increase of mechanical adhesion could be received, which is unattainable by conventional methods.

Tests of laser cleaning of patina covered copper surface were carried out at laboratory conditions (Fig. 6). A TEA CO_2 laser working at different energy density was used. Application of 4 J/cm^2 energy density resulted positively in cleaning from patina (Fig. 6).

a) b)

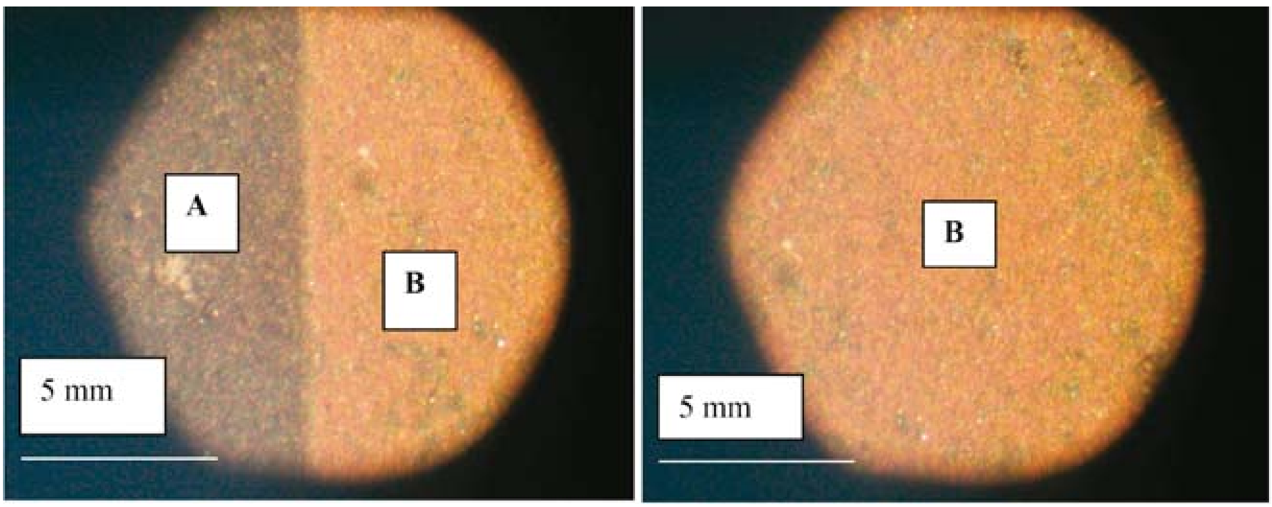
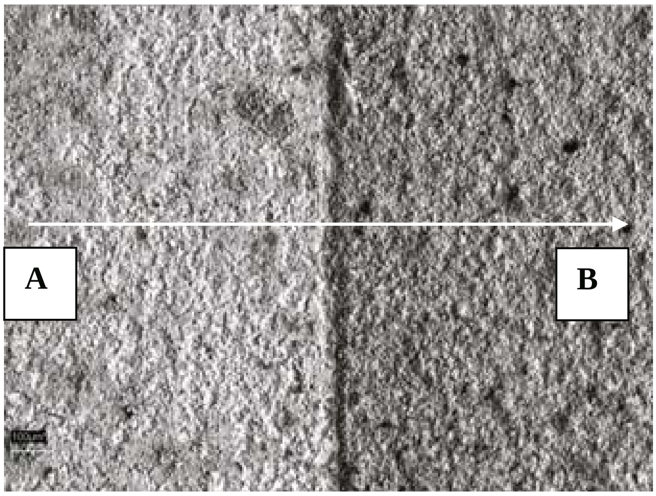


Fig. 6. Copper covered with patina cleaned with TEA CO_2 laser with energy density of laser beam of 4 J/cm^2 , pulse duration 150 ns (5 pulses); a – surface before cleaning (A), b –interface of cleaning (A and B), c – after cleaning (B)

A qualitative X-ray microanalysis, along A-B line (Fig. 7 - left picture) in the cleaned zone, revealed removing of Si, Fe, C, S, which is a positive effect. This lad to uncover of copper substrate (Fig. 7 - right picture). By application of double smaller energy density i.e. 2 J/cm^2, not satisfactory results were obtained by patina cleaning.

a)



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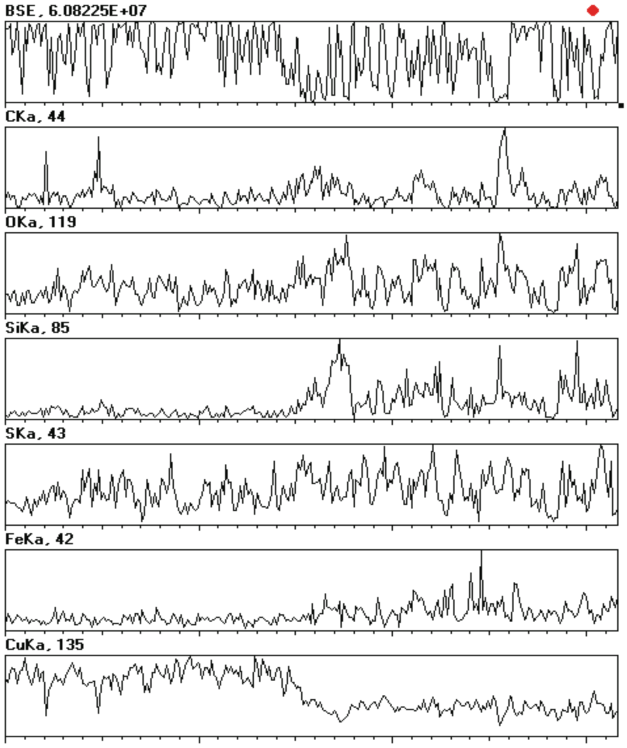

Fig. 7. Surface of copper covered formerly with patina and laser cleaned using TEA CO_2 laser with energy density of laser beam of 4 J/cm^2 , pulse duration 150 ns (5 pulses); left picture – view of surface before cleaning with patina (B) and after cleaning (A); right picture – result of qualitative X-ray microanalysis along A-B line (marked on the left picture)

Cleaning of a black lacquer coat using Nd: YAG laser was carried out in the frame-work of experiments. The coat was sprayed by a powder method on aluminium alloy substrate. Energy density of 13 J/cm^2 caused immediate cleaning with partial melting of the cleaned surface (Fig. 8). Application of lower energy density in the range of 4 to 6 J/cm^2 gives satisfactory cleaning results without partial melting of the substrate.

a) b)

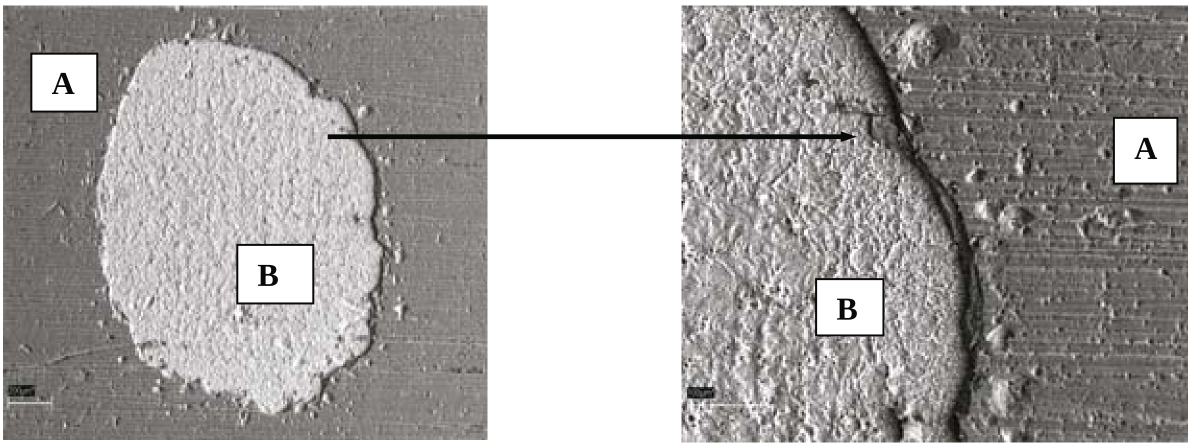

Fig. 8. Characteristic zones of aluminium alloy surface layers covered formerly with black lacquer coat using spray powder method and subsequently cleaned using Nd: YAG laser with energy density of laser beam of 13 J/cm^2 , pulse duration 150 ns; left picture (a) – cleaned zone (3 pulsed), right picture (b) – topography after cleaning; A - black lacquer coat, B – after cleaning, micro cracks visible

Examples of the laser cleaned elements of machine, namely, engine piston, piston rings, engine valves and welded support are presented in Fig. 9. Application of pulsed Nd: YAG laser with energy density of laser beam of 2 J/cm^2, pulse duration 10 ns gave good promising results and chances for industrial application of this technology.

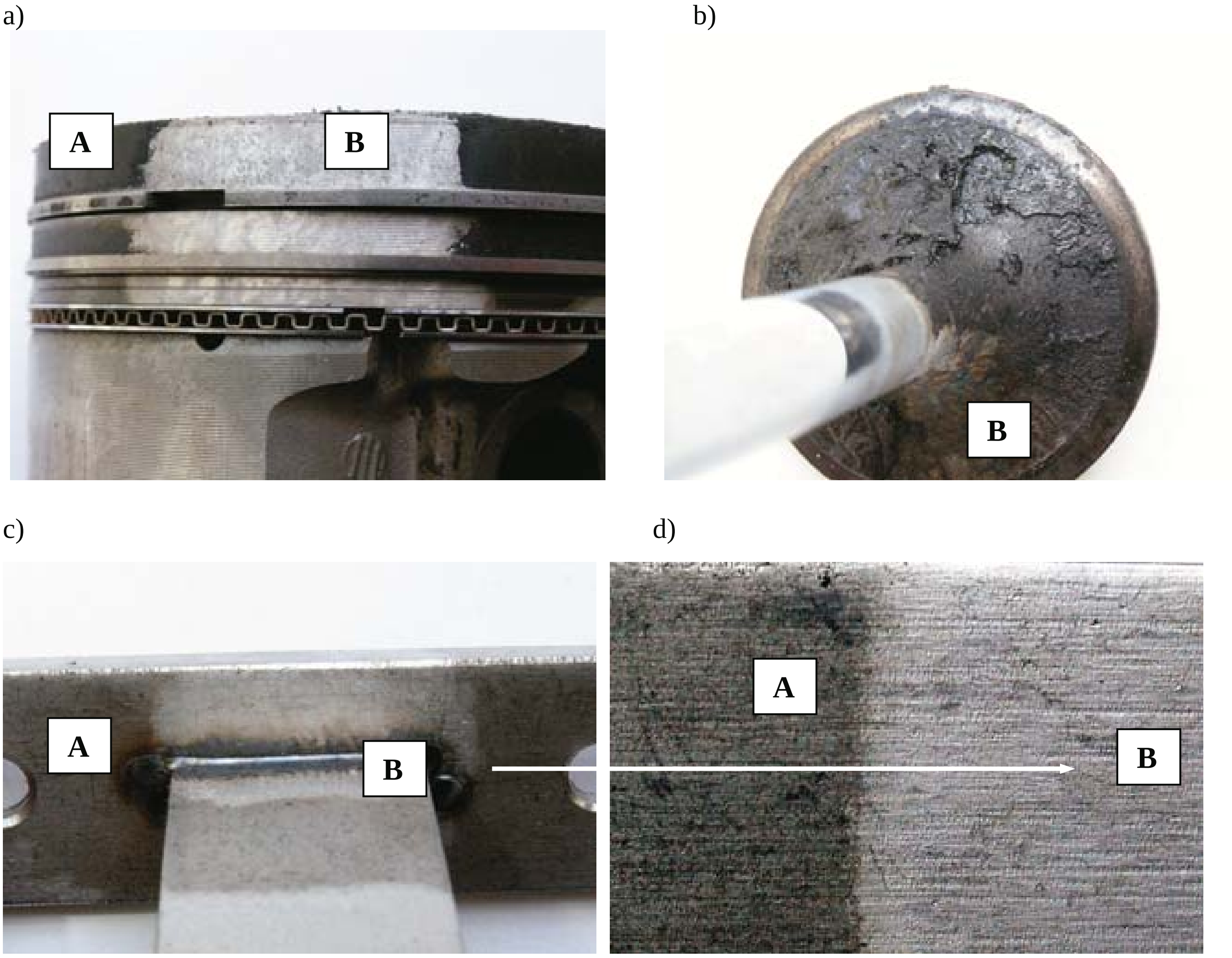

Fig. 9. Examples of technological application of laser ablation cleaning of machine elements; engine piston, piston rings, engine valves and welded support; Nd: YAG with energy density 2 J/cm^2 and pulse duration 10 ns; A – before cleaning, B – after cleaning

5. Summary and conclusions

Laser cleaning of surface layer of materials has a huge superiority in respect to the till applied conventional methods. It is very effective and moreover non-contact, universal and safe.

Main features of the method comprises in:

- it is friendly for environment,
- it has small influence on the substrate,
- it gives selective exposition of non-cleaned surface,
- it makes application in any place,
- it is effective and safe.

Very good technological prospects are opened for ablative laser micro- and nano-processing in surface engineering. Laser processing is mainly used for removal of contaminations, physical and other encrustations deposited on materials and machine elements, and next for obtaining of metallically clean surface layers of a specified surface topography and condition used for improvement in adhesion of surface layers produced in modern surface engineering (painted, cemented, or thermally sprayed coatings, or surface activation before thermochemical treatment (for example – glow discharge or controllable gas nitriding) or PVD/CVD processing.

Obtained micro- and nano-layers have specific usable properties, much better than surface layers or coatings systems commonly used in the market or industry. In result of ultra-fast laser modification a specific material properties can be obtained – a high wear, abrasion, and corrosion resistant surface layer of a very high hardness.

There exist many techniques for surface removal and cleaning but a few of them fulfils economic and environmental demands. Laser processing of a surface fulfils or even exceeds requirements coming from electronics, atomic energy and aerospace industries, and civil engineering. Three types of the most frequently used lasers offer characteristic advantages understood as average power, pulse operation, wavelength, optical feedback with material processed, and fibre delivery.

The most important is knowledge about laser-matter interaction which is needed for correct development of process parameters. Knowledge of energy absorption, heat transfer, and reflection coefficient is, in turn, very helpful for recognition of what phenomenon predominates (heat treatment, melting, or vaporization).

In order to remove closely attached layers laser ablation is necessary. Ablation is obtained via thermal shock, melting, and evaporation. Paint, oxide, organic/inorganic, and other thin substrate layers can be removed.

The process of surface layer cleaning of materials and machine elements can be carried out in various ways. In general, when using pulse laser radiation, five different mechanisms of removal of particles, encrustations, or coatings can be applied. So, the process of removal can be performed via following physical processes: surface vibrations, particles oscillations, thermal expansion of particles (or encrustation), generation of so called detonation wave over surface being cleaned, and laser ablation.

Lasers are especially useful for removal of layers from many types of substrates like wood, metals, plastics, composites, stones, ceramics, leather, and others.

The important advantage of laser cleaning and surface modification is the capability of processing automation which is related to process repeatability, ease of parameters controlling, possibility of strengthening in zones difficult to access, high precision of interaction and high efficiency as well.

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