Abstract

Pulsed and continuous wave lasers, which are widely applied in diverse micromachining industrial processing, could be used in the cleaning of historic objects. However, many issues concerning the interaction between lasers and historical metals are not yet resolved and the application of lasers in metal conservation is not universally accepted. As a substantial part of a broader project, this paper presents the preliminary evaluation of critical process issues, including diagnostics of corrosion layers, their ablation thresholds as well as evaluation of the influence of laser radiation parameters (pulse duration, laser fluence) on post-process surface properties.

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1. Introduction

Due to the number of aggressive substances in the environment and atmosphere, metal works of art are subject to the process of corrosion and oxidation whether they be in contact with the earth, water or the air. This does not only apply to metal artifacts found in archeological digging sites or discovered in the sea, but also to artworks that are exhibited in polluted surroundings. For the purposes of stabilizing the condition of the items and preventing any deterioration, the encrustations that are there should be removed before protective coatings are applied.

The conventional methods for cleaning metal artworks are based on mechanical and chemical removal of the built up layers. They require a great deal of skill, and are time consuming and are not fully controlled. They
also entail the disposal of waste and chemical substances that may be harmful to the environment. An alternative method is laser technology that in comparison with conventional methods provides automation, selection, precision and most importantly a high level of control in conjunction with various “in situ” analytical laser techniques.

The process of cleaning works of art by laser was first demonstrated in the 70’s [1], and is currently accepted as a method of conservation [2]. However discussions concerning where the limits are in the use of laser technology for the removal of unwanted surface layers are always taking place. This in particular pertains to the conservation of metals, due to the unresolved issues related to the preservation of the original surface, knowledge on the formation of unwanted laser-induced changes or changes to the morphology after laser irradiation [3,4]. This goes against the principle requirement of every conservation intervention which requires that the item be restored to its original unaltered condition. In practice this is seldom possible to achieve, because it means that it is not possible to carry out any experiments on the items being restored. This is what differentiates materials engineering and the science of conservation. The phrase “optimal laser cleaning of artworks” does not only refer to quality and economic parameters (efficiency, effectiveness, speed), but most importantly - the safety of the irreplaceable artworks during conservation.

Preservation of the undamaged surface of the artworks during the laser cleaning is associated with the selection of the optimal process parameters and above all the radiation wavelength, energy density and length of the laser pulse and also the environment in which the radiation is taking place. These factors directly affect the thermal and photomechanical phenomena that are associated with the radiation interaction with the encrustation and metal substrate.

It is common knowledge that the interaction of long laser pulses with a solid in a free running regime causes the generation of intense heat on the worked surface. This in turn causes it to melt and often also boil [5]. However, transient temperature rise accompanies also nanosecond pulses generated in the Q-switched regime, causing localized melting of the surface. As stated in [6], an increase in the length of pulse with a small energy density of 0.15 J/cm² from 6 ns to 100 ns causes a reduction in the peak temperature from over 450°C to below 150°C. It is also known that the photomechanical effect induced by the Q-switched regime generates pressure pulses (shock waves) with amplitude of up to hundreds of bars [7]. This can cause mechanical damage to the surface of delicate artworks, and most importantly to their artistic surface covering. An extended length of pulse reduces the pressure spike, and in the case of microsecond pulses practically do not cause any thermal stresses to act on the substrate material [8]. Wetting the surface of the object prior to cleaning lowers the ablation threshold of the encrustations [9]. This allows lower energy densities to be used and, as a consequence, reduces the thermal and mechanical effects of the laser radiation pulses. The cleaning process relies on the use of an appropriate thickness for the layer of liquid and an appropriate laser energy density [10]. Cavitation can readily occur if the layer of liquid is too thick, the process becomes inefficient and collapse of cavitation blisters causes high pressure spikes which can damage the treated surface [6].

2. Selected results of numerical simulation

The encrustation on historical structures and artworks often has a porous structure which causes the adsorption of gasses and water. As mentioned in the introduction, this phenomenon significantly changes the physical characteristics of the material and plays an important role in the laser cleaning process. Based on the numerical modeling of laser ablation widely presented by authors in other publications [11,12], computer simulation of the removal of encrustations in the presence of water was carried out. Fig.1a shows the thickness of the evaporated layer of graphite (that imitates the encrustations) from a solid substrate (aluminum plate) as a function of the laser pulse energy. It has been assumed that the pores in the graphite may be filled with air (dry cleaning) or water (wet cleaning).

It may occur that the water does not penetrate the porous encrustation structure, and a layer of liquid remains on the surface. This results in the creation of an inert layer with a density similar to that of the deposited encrustations, causing a significant increase in the amplitude of the pressure pulse. This is illustrated in Fig 1b. When calculating the effect of the inert layer on the amplitude of the pressure pulse it has been assumed, that the absorption layer is solid graphite 3 µm thick, and the work piece is again aluminum with a thickness of 0.6 mm chosen for simplicity. Calculations have been made for times of up to 100 ns, which is why the pressure pulse does not reach the bottom
wall of the sheet. The calculations presented in Fig.1 demonstrate that water can significantly increase the effectiveness in removing porous encrustations. However, if the layer applied is too thick, it can cause an excessive increase in the pressure pulse amplitude on the substrate being cleaned and cause damage to it.

![Figure 1](image1.png)

**Fig. 1.** (a) Influence of graphite porosity [%] on the thickness of the graphite layer removed from an aluminum substrate as a function of laser pulse energy density. Pores filled with air or water. Width of laser pulse – 5 ns, graphite layer thickness – 3 μm; (b) Influence of water inert layer on the shape of the pressure pulse propagating inside an aluminum substrate after 25 ns and 100 ns from the beginning of the laser pulse. Laser fluence 10 J/cm². Width of laser pulse 10 ns (FWHM)

A detailed theoretical analysis of the effect of the laser pulsewidth on the transient temperature increase of the substrate, using typical laser cleaning process parameters on gilded metals was presented in the works of Siano et al. [6]. Here, it was noted that local surface melting could occur due to the action of typical nanosecond pulses generated in the Q-switched regime. This was confirmed by the microscope photos of the surface after being cleaned by laser. Presented below are the results of our numerical simulation of this phenomenon, based on the analysis of laser irradiation of a 4 layer material sample presented in Fig.2 [17].

![Figure 2](image2.png)

**Fig. 2.** Theoretical simulation of the geometry of laser pulse illumination on a four-layer sample

![Figure 3](image3.png)

**Fig. 3.** Temperature distribution inside four layers illuminated with two values of laser power densities for 10 ns long laser pulse. Power densities and fluences are given at individual plots [17]

The theoretical sample consists of chromium (Cr), copper (Cu), aluminum (Al), all 100 nm thick, superimposed onto a 3 mm thick quartz substrate. The chromium layer has been selected to simulate a higher melting point than
for gold and silver. The calculation parameters guaranteed a rise in temperature of the illuminated outer layer below the melting point of the material while the behaviour of the underlying layers was analyzed. Selected, calculated distributions of surface and intrinsic temperatures are shown in Fig.3. Fig.3b shows that laser pulse power density of over $1.5 \times 10^7$ W/cm$^2$, around 30 ns after the laser pulse caused melting of Cu and Al bottom layers, leaving the Cr surface layer intact. Melting points of metals and quartz ($T_m$) are shown as short horizontal lines.

Geometry of the four-layer configuration shown in Fig.2 has been reconstructed in a real experimental model. Samples were prepared using classical vacuum deposition of thin metallic layers. Average thickness of metal layers, determined by the scanning transmission electron microscopy - STEM - were: Cr – 40 µm, Cu – 250 µm, Al – 100 µm (Fig. 4). Laser irradiation caused irreversible damage (melting and reciprocal diffusion) of Cu and Al layers, causing micro-explosions of gas bubbles at the Cr surface. The Cu/Al reaction is confirmed by the second STEM characteristic, shown in Fig. 4b as orange Cu and deep blue Al dashed lines. Areas connected with the stress caused by the explosion and varied thermal expansion of materials, can be seen around the hole, presented in the small SEM photograph (upper-right corner).

![Fig. 4. STEM picture at perpendicular cross-section and linear analysis of chemical composition across the layers [17]](image)

### 3. Description of the tested objects

For the purposes of testing the laser cleaning process, two copper pieces from historical items (Fig. 5) were prepared, one extracted from the roofing on the Palace in Wilanów from the turn of the 19th/20th centuries and the other being a wing from a bronze metal gilded putto from the Wilanów Palace gardens façade decorations, dated as from the end of the 17th century and claimed to be the work of the Dutch sculptor Disqenue from his atelier in Rome.

![Fig. 5. Photographs of the examined historical objects: (a) samples of copper roofing from the Wilanów Palace in Warsaw; (b) gilded bronze putto with laurel from the Wilanów Palace gardens façade](image)

Plates cut from Wilanów Palace copper roof covering are an ideal test material not only due to the quantity and the excellent state of preservation of the many years of weathering, but also due to the possibility of conducting
destructive tests and applying cleaning processes utilizing a wide range of laser parameters, up to a time when significant changes to the surface are achieved. The bronze putto is an example of a gilded metal artwork. It has layers of grime and atmospheric contamination. It also shows signs of local corrosion of the metal beneath the gold layer and has numerous signs of mechanical damage.

Small fragments of both items have been cut out of representative encrustation areas and have been embedded in Meliodent resin and polished. The micro-sections were subjected to further analytical testing. The elemental composition of the encrustations was tested using a scanning electron microscope with energy dispersive X-ray probe (SEM EDS) and laser-induced breakdown spectroscopy (LIBS). SEM EDS testing was conducted using a HITACHI S-3500N microscope, taking into account the topographic analysis in SE mode (Secondary Electrons - surface shape) and BSE mode (Back Scattered Electrons - for element distribution), and energy dispersive X-ray spectroscopy of the sample of elements in selected points. The LIBS analysis was conducted with the use of an ESA 4000 (echelle type) spectrometer with a ICCD Kodak K1001 camera to analyze the plasma generated by the laser pulses from an Nd:YAG model Brio (BigSky/Quantel), working in the fourth harmonics with a basic wavelength of 266 nm, with a pulse energy of 11.2 mJ and pulse length of 4 ns. In addition to the LIBS quality analyses, a quantitative stratigraphic LIBS analysis based on the calibration characteristics registered for the sample metal pieces that had been exposed to similar experimental conditions was carried out. An identification of the chemical compounds present in the encrustations was carried out using a Raman Nicolet Almega spectrometer fitted with two sources of laser radiation (532 nm and 780 nm) and a confocal Olympus BX microscope. Further tests were carried out using a Phillips 1830 X-ray diffractometer fitted with a X-Pert goniometer (CuK radiation) and a FTIR Perkin Elmer 2000 spectrometer (with a resolution of 2 cm⁻¹). A more detailed description of the parameters, used equipment and the experimental conditions can be found elsewhere [13,14].

The surface encrustation structure and the cross section are presented in the SEM photos in Fig.6. The total average thickness of layers 1 + 2 (Fig. 6b) amounts to approximately 65 μm, and in the external part the presence of alumino-silicate particles up to 30 μm in size can be seen.

![Fig. 6. SEM photographs of encrustation on copper sheets in BSE mode: (a) top view; (b) cross-section](image)

Raman Spectra of clearly separated layers, originally brown-red (1) and green (2) in color, visible in the figure, allow for the identification of cuprite Cu₂O and brochantite Cu₄SO₄(OH)₆. This is in conformance with the information available from literature about the typical course of change in the surface of copper during long-term reactions to the atmosphere [15]. The presence of brochantite was confirmed through analysis with an FTIR spectrometer, and the presence of cuprite and brochantite was confirmed by analysis carried out with an X-ray diffractometer. The latter results also allowed for the discovery of trace amounts of antlerite Cu₃(SO₄)(OH)₄, hydrogen sulfide H₂S, paramelemacite Cu₄O₃ and copper carbonates (such as malachite and azurite). The encrustations are brittle and contain numerous cracks which may have been developed during the preparation of the sample for analysis.

In depth distributions of three selected elements: Na, Al and Ca in the encrustations determined by the LIBS method on the basis of normalization in the intensity of the spectral lines Na I 589.59, Al I 394.40 and Ca I 445.48 to the spectral intensity of CuI 510.553 nm (sample substrate) are presented in Fig.7a. The sample depth was measured by the number of laser pulses that affected the same place. Depending upon the structure of the material, a
layer of 5 to 10 μm in depth was ablated. This means that the excess calcium quantity is present in a layer up to 100 μm in depth, and the whole black layer (with a varying concentration of Na and Al) has a maximum depth of 300 μm (30 laser pulses). It is interesting to note the respective changes in the surface value of lead content (Fig.7b) in comparison to identical measurements carried out for the sample of roofing material from the Karol Poznański Palace in Łódź. This palace is situated at an intersection of high-traffic roads in the centre of the city and a significant increase in the concentration of deposited lead can be attributed to the decades of exhaust fume emissions from automobiles.

Fig. 7. LIBS stratigraphy of encrustation on copper sheets: (a) normalized content of sodium, aluminum and calcium; (b) comparison of normalized lead content in a copper sheet from the Wilanów Palace in Warsaw (garden) and the Karol Poznański Palace in Łódź (street)

The base metal of the putto figure with a torch is a copper-zinc alloy (with 11 – 20 % of zinc) and a small quantity of added lead (0.2 – 1.4%). The differences result from the use of different materials for individual elements of the putto (body, wings, torch). Stratigraphic testing has highlighted the elementary black encrustations similar to those found on the copper sheets. The structure of the layers has been presented in the polished cross section (Fig.8a) and LIBS stratigraphic measurements (Fig.8b). Raman spectrometric measurements identified the existence of antlerite Cu₃SO₄(OH)₄ and cuprite Cu₂O. The grey compounds visible in the small photo in the top right hand corner of Fig.8a are most probably silver compounds (sulfides). While these were not identified in the Raman spectra, the ions S⁻² and Ag⁺¹ were discovered in the course of the micro chemical analyses. The black layer deposited on the undamaged gilding is significantly thinner and does not exceed 50 μm. This is equivalent to 5 laser shots in the LIBS measurement. The preliminary increase in the respective concentrations of Au and Ag is associated with the removal of deposits (Ca among others). The resulting quick drop in the Ag and Au curves is due to the thin nature of these layers (10 – 20 μm).

Fig. 8. Layered structure of the bronze putto surface: (a) cross-section; (b) LIBS stratigraphy of main elements (gilding, substrate and Ca)

4. Laser cleaning tests

Laser cleaning tests of the copper sheets were conducted using long pulses ranging from 100 μs – 1 ms that were obtained by the Nd:YAG laser in free running regime, and also using short nanosecond pulses generated in the Q-
switched regime. Several hundred irradiations were carried out using various pulse lengths, laser energy densities and varying amounts of irradiation on the same sample area. Typical photographs for the irradiation results are shown in Fig. 9.

The samples after laser illumination were examined using a scanning electron microscope HITACHI S-3500N equipped with EDS. The investigations included observations in SE and BSE modes and point analyses of the chemical composition by EDS. The EDS measurements were performed at 15 kV for 60s.

The laser-deposit interaction in the long laser pulse range resulted in melting, evaporation and sputtering of the surface layer. The investigations demonstrated that in the case of a single laser pulse the substrate surface was not uncovered. The smallest laser energy density in the range of 1.2 – 1.7 J/cm² didn’t change either the morphology or the chemical composition of the deposit in the X-ray spot region. A step increase in energy density resulted in more evident melting and eroding of the deposit surface. The strongest evidence of melting was exhibited in the samples illuminated with the longest laser pulses of 1140 µs (Fig.10a,b), however SEM EDS measurements showed a decrease in the sulphur content in the cleaned region, locally to 1-2 wt.% (probably due to the removal or decomposition of brochantite).

Illumination with multiple laser pulses resulted in the removal of the deposits and melting of the copper substrate surface. On the uncovered copper surface large blisters, of up to 250 microns were observed. The substrate/copper surface was oxidized, the oxygen content varied in the range from 4 to 20 wt.%.

In the case of pulsed irradiation within the nanosecond range, a significantly smaller amount of local melting of the surface was noticed (Fig. 10c), replaced with a selective, sequential removal of the deposited material. SEM analyses of the cross section clearly showed the cleaning and gradual sequential reduction in the thickness of the cuprite oxide layer, however even in this case the blackening of the uncovered copper substrate was observed when more than 10 laser pulses were applied (Fig. 9c). Analyses showed that there was no change in the morphology (melting) of the copper substrate. An increase in the porosity of the oxide layer was observed together with the
increase in the number of laser pulses. This is characterized by the mean arithmetic deviation in the roughness profile $R_a$ (1.95 μm for 6 pulses and 3.50 μm for 10 pulses). Analyses of the material samples for the blisters (Fig.10c), collected with a focused ion beam (FIB) system showed their relationship with pores present in the oxide layer (Fig.10d). There were no significant changes in the morphology of the surface when the duration of the pulses was increased from 6.2 ns to 17 ns.

The testing of laser cleaning of a bronze putto was carried out using a small ReNOVALaser 1 Q-switched system operating at 1064 nm. This system delivers a maximum of 120 mJ per pulse with a variable repetition frequency from 1 to 20 Hz. The pulse width was approximately 6 ns and the beam profile had a top-hat energy distribution at the output of the optical fiber beam delivery system. Testing was carried out on the external side of the right wing of the putto with the laurel. The locations of the treatment and laser cleaning methods are shown in Fig.11a. Cleaning with minimum fluence means the application of a laser energy density just above the predetermined threshold of encrustation ablation (0.18 J/cm$^2$ – “wet” and 0.45 J/cm$^2$ – “dry” laser cleaning in Fig.11a). If energy above the minimum fluence is used, i.e. without specific limits, it should be self-limiting and once the surface is clean the energy should be reflected from the cleaned surface and the laser ablation rate drops instantly (so called self-limiting laser cleaning). Laser fluence was not measured in this case.

![Image](image1.png)

**Fig. 11.** (a) Putto wing with marked areas of different laser treatment procedures; (b) SEM photographs of putto wing surface characteristic areas selected after wet laser treatment with minimum fluence

![Image](image2.png)

**Fig. 12.** SEM image (a) and composition (b) of melted fragment of area 6 (Fig.12a)

The evaluation of the cleaning tests was carried out using a scanning electron microscope with an EDS spectrometer. The EDS measurements were performed at 15 kV of acceleration voltage. Microscopic observations of all areas enabled two characteristic morphologies of the cleaned surface to be distinguished. The first includes areas numbered 1, 2, 7, 8, 11 and 12 in Fig.11a. In all locations laser cleaning revealed gilding or the putto surface. Parts of areas revealed a smooth surface of the gilding (Fig.11b), composed of gold with up to fifteen percent of silver and copper. In areas covered with droplets mainly copper was detected. This probably indicates the melting of...
the top surface layer down to the substrate, conforming with the theoretical results presented earlier. The unveiled areas also contained numerous cracks, discontinuities and corrosion cavities. Inside the pitting, sliver with copper and oxygen additions were detected.

Much worse results were obtained for unlimited laser fluence on areas 5 and 6 in Fig.11a. In these locations, the laser treatment uncovered the gilding or the surface, however the surface of the gilding was remelted. The strongest melting occurred in area 6, where the formed layer consisted of gold and silver (50:50).

5. Laser system with adjustable pulse length

For the purposes of increasing and tuning the laser pulsewidth during operation [8] it has been proposed that replaceable optical fibers of various lengths be used in the Nd:YAG Q-switched laser resonator. Pulses that vary from tenths of a nanosecond to several microseconds were achieved. The constructed laser device was used for the cleaning of an unique monument in Florence, the gilded bronze panels from the Porta del Paradise – the eastern doors of the Cathedral [6]. Adjustment of a laser with optical fibers to a specific cleaning procedure in the case of a specified metal object requires a reconstruction of the system (change the optical fiber length). A better solution seems to be the achievement of an adjustable pulsewidth based on the appropriate construction of the unstable resonator and the adjustment of the excitation lamp power parameters, as well as establishing an appropriate output energy with a two and three stage laser amplifier. This set up would allow for the control of the pulsewidth generated during the course of conservation works "in situ". The first step in this direction was a system with a stable resonator generator, as shown in [16]. A diagram of a new proposed solution with an unstable resonator and an electro-optical system that separates the laser pulses is presented in Fig.13.

In the unstable generator system from Fig.13 an almost fully adjustable laser pulsewidth from 100 to 1000 ns was achieved. Due to a lack of space in Fig.14 only the shape of several energy pulses with output energy of several mJ has been shown. The amplitudes shown don’t correspond to the real values of laser output energy because of different levels of radiation attenuation in front of photodiode.

Fig. 13. Optical scheme of the laser oscillator-amplifier system

Fig. 15. Oscillograms of selected laser pulses: a) \( \tau = 232.2 \) ns; b) 500.5 ns; c) 760 ns; d) 931.3 ns
6. Summary

As it has been shown in the experimental section, the use of a laser generating long pulses in the range of 100 μs – 1 ms, leads to irreversible damage to the layers of cuprite and/or to the typical copper substrate used in historical roof coverings. This disqualifies use of the Nd:YAG pulse laser in a free running regime for the cleaning of metal artworks. In the case of a delicate gilding (bronze putto) typical nanosecond pulses (6 – 17 ns) generated in the Q-switched regime of the Nd:YAG laser would also cause local damage and surface melting to the gold layer just below the boundary of the soiled surface ablation, even if the minimal energy density of the laser was used. These facts make it necessary to be extremely careful when selecting the duration of the laser pulses in the ranges of tens and hundreds of nanoseconds when the metal work piece cannot be subjected to high mechanical stress or large instantaneous temperature gradients. It may also be helpful to carefully use a liquid as an absorption layer on the surface of delicate metal artworks.

A straightforward design solution has been proposed for the development of an unstable laser oscillator – a two stage amplifier, where continuous adjustment of the pulsewidth from 100 – 1000 ns is possible. Basic experiments directed at the optimization of work and control of the complete system as well as the laser cleaning tests are planned for May or June of this year. The results of these tests will be presented during the 2010 LANE Conference.

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