

Pulsed laser cleaning of metallic heritage

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Abstract. The main goal of this study is to design and optimize a low-invasive laser cleaning treatment for metallic cultural heritage artefacts. The treatment should remove the dangerous corrosion products without affecting the original surface of the artefacts. The pulsed laser cleaning process is performed, in this preliminary step, with a near-IR Q-switched Yb:YAG fibre laser on artificially patinated Cu-based reference samples.

A morphological and microstructural investigation has been carried out on the specimens submitted to the cleaning process in order to evaluate the effects of the different laser parameters.

The optimized laser cleaning procedure will be validated, in a second step, on real ancient metallic artefacts.

I. INTRODUCTION

In Cultural Heritage conservation field, laser-based techniques are widely used as advanced tools for cleaning artefacts surfaces. As a matter of facts, laser cleaning may be controlled with high precision, thus reducing the risks of damage of the underlying material. Correctly applied, laser cleaning can minimize or avoid both mechanical and chemical disruption of historic surfaces, and in certain circumstances, can selectively remove contaminating dirt or coatings. Initially laser beams have been utilized for cleaning of stone sculptures and paintings, but subsequently other classes of artworks have been treated, as metals, fossils, bones, wood, leather, paper, etc.

Dealing with metallic artefacts, the laser cleaning technique has been applied mainly on copper-based samples in order to remove the dangerous corrosion products without affecting the protective oxide layers [1; 2; 3]. However, further research is needed because for optimizing the results the laser parameters have to be set as a function of the corrosion products layers.

Unluckily the corrosion mechanism of Cu-based ancient artefacts buried in soil is very complex and gives rise to stratified multilayer structures [4; 5]. The patinas of stable artefacts are characterized by a tin and/or copper oxide layer directly in contact with the original surface able to

protect the metallic substrate by a further corrosion. Meanwhile, in aggressive environments, other typologies of patinas may be found: they often contain dangerous chlorides ions that can destroy the original structure of the metal altering the feature of the artefact itself [6; 7].

Since archaeological artefacts are valuable objects, the new cleaning procedures have to be tested, in a first step, on simulated samples and only the optimized one may be validated on real artefacts. Consequently, in this study, in order to design a low invasive and self-limiting laser cleaning treatment which allows to remove the dangerous corrosion products without affecting the original surface, the effect of the laser parameters has been tested on artificial patinas grown on reference copper specimens.

The study was carried out performing the cleaning with a pulsed laser in dynamic condition on the surfaces of copper reference specimens artificially patinated, by means of a chemical method and of an electrochemical process. The evaluation of the effects of the laser parameters has been performed by means of morphological and microstructural analyses on the treated surfaces before and after the cleaning procedures.

II. MATERIALS & METHODS

A. Materials

Two kind of artificial patinas have been produced on Cu 99.96 wt%, reference samples (45x15x5 mm). The specimens were polished with 500 to 4000 grid SiC paper, rinsed in ethanol in ultrasonic bath for 5 min, and well dried. On a set of samples, an electrochemical patination was performed in 0.1 M Na₂SO₄ solution at room temperature [8] in order to obtain an oxide layer. On another set of samples, a chemical synthesis was performed by immersion in a 0.5 M NaCl solution for two months at room temperature in order to obtain a chloride patina.

Knowing that a laser is a light amplification by stimulated emission of radiation, interaction as absorption, diffusion or both may occur with the materials and, due to the power used, also thermal interactions have to be taken into

account. Consequently, the first important laser parameter to choose is the laser wavelength.

In order to obtain a low invasive and self-limiting laser cleaning treatment (Fig. 1) and knowing from reflectance measurements that bronze reflects and patina absorbs in the infrared region, a laser operating in the near-IR region has been chosen.

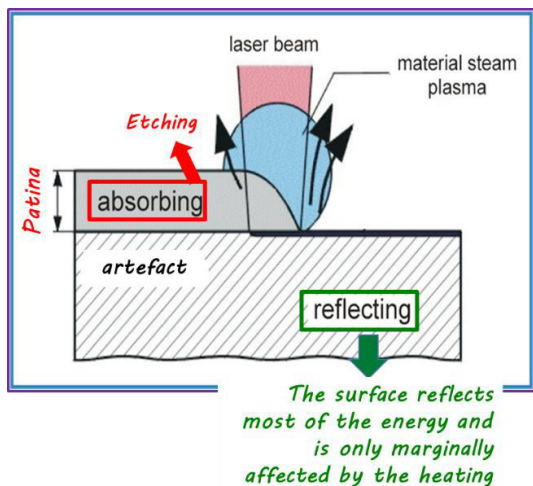


Fig. 1. Self-limiting laser cleaning treatment.

The laser is a Yb:YAG fibre laser (model EasyMark-20 from Jeanologia), operating in the near-IR at a wavelength of 1064 nm. Laser pulses are generated in a Q-switching regime, with pulse duration in the range 4 - 200 ns, delivered by means of two-galvanic mirrors and focused with a f-Theta lens with 160 mm of focal distance. The laser system is coupled with EzCAD 2.1 UNI, a vector graphic editor, with a CAD-like capability that allows to perform rapid, precise and complex surface scanning treatments (Fig. 2).

B. Methods

In this study the laser-material interactions have been evaluated varying the laser parameter values in terms of pulse duration and power (fluence and irradiance). The *fluence* is the pulsed power per area, whereas the *irradiance* is the average power per area; the irradiance strictly depends from the pulse duration.

In particular, a short *pulse duration* means a high irradiance and consequently a low penetration of the laser thermal effect and a high interaction laser-patina. The use of a short pulse duration means to perform a treatment more aggressive with respect to the patina.

The evaluation of the laser-material interactions and of the behaviour of the two artificial patinas was carried out from a morphological and microstructural point of view by means of different techniques. The surfaces of the specimens before and after the cleaning treatments were analysed by means of X-Ray microdiffraction (μ XRD, D-

MAX Rapid Rigaku instrument), field emission scanning electron microscopy (FESEM, Zeiss, Supra40) and confocal microscopy (CM, SensofarPL μ 2300).

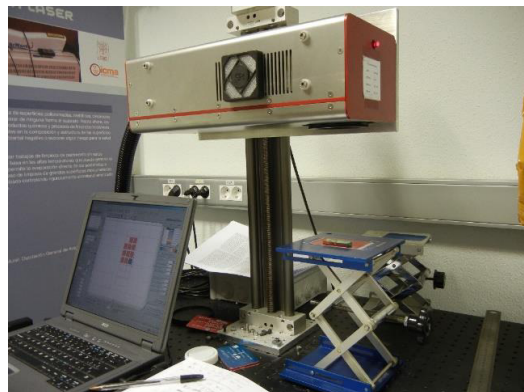


Fig. 2. Laser system used coupled with EzCAD 2.1 UNI.

III. RESULTS

The microstructural analysis confirmed that the electrochemical patina (*oxide patina*) is mainly composed of cuprite (Cu_2O), whereas the chemical patina (*chloride patina*) is mainly composed of paratacamite ($\text{Cu}_2\text{Cl}(\text{OH})_3$), with the presence of cuprite (Cu_2O) and copper chlorides, as CuCl_2 .

From the screening treatments performed, the most promising results were obtained using short pulse duration (4 ns - laser cleaning A) and (8 ns - laser cleaning B) and low output laser power (Tab. 1).

Tab. 1. Experimental parameters employed for the laser cleaning treatments.

Laser Parameters	Laser cleaning treatment	
	A	B
Power, P [W]	0.23	0.21
Fluence, F [J/cm^2]	1.63	1.48
Irradiance, I [MW/cm^2]	406.73	185.68
Pulse duration, t_p [ns]	4	8
Scan speed, v_{scan} [mm/s]	300	300
Repetition rate, f_{rep} [kHz]	20	20

A different behaviour of the two artificial patinas was observed, from a morphological and microstructural point of view, when the specimens were submitted to the same pulse duration conditions.

For the oxide patina, CM and FESEM images evidence an original morphology of the patina very rough (Fig. 3).

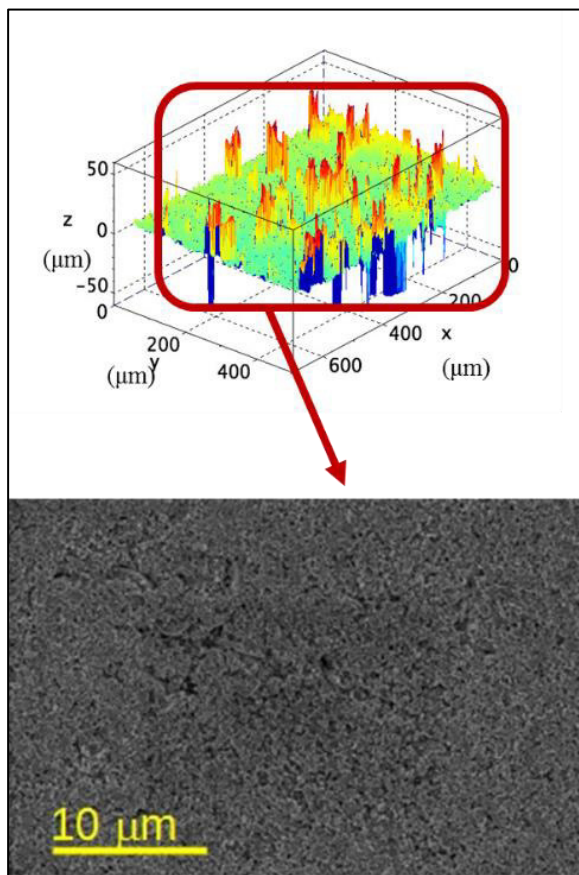


Fig. 3. CM (up) and FESEM (down) images of the original oxide patina.

After the 4 ns treatment, the morphological analyses evidence a strongest interaction laser-patina under short pulse duration condition (laser cleaning A): the treated areas present a smoother surface compared to the non-treated areas associated with a 2 μm-reduction patina and a slight surface melting (Fig. 4).

The μ-XRD spectra on the area of the oxide patina treated with the laser cleaning A, evidence a slight increase in the relative intensity of the metallic copper peaks in comparison with the relative intensity of the copper peaks of the untreated oxide patina (Fig. 5).

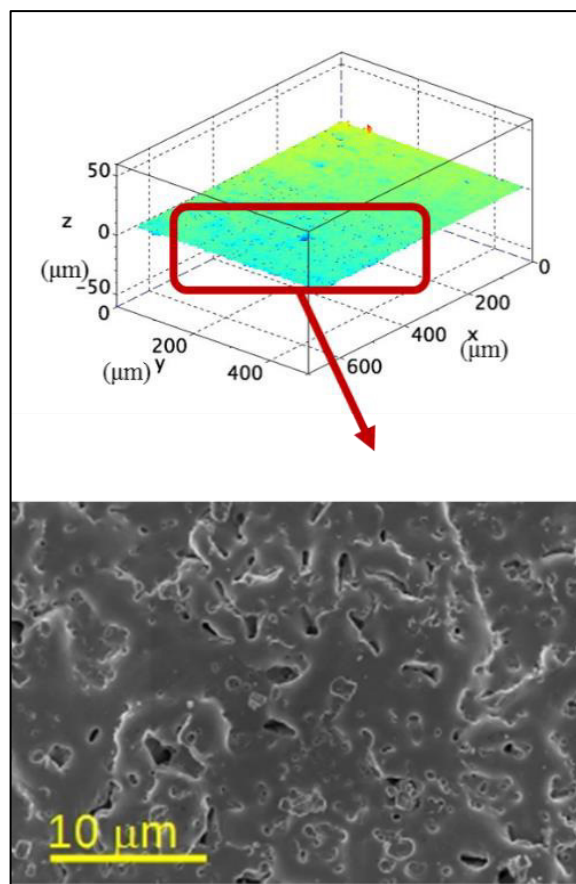


Fig. 4. CM (up) and FESEM (down) images of the 4 ns-laser treated oxide patina (laser cleaning A).

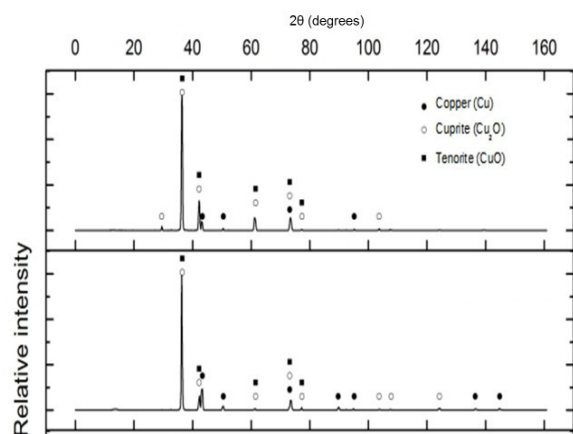


Fig. 5. μ-XRD spectra of the original (up) and 4 ns-laser treated area (down) oxide patina.

A different situation was present on the chloride patina before the laser cleaning treatment: CM and FESEM images show a high homogeneity in thickness of the original patina with the presence of big crystals (Fig. 6).

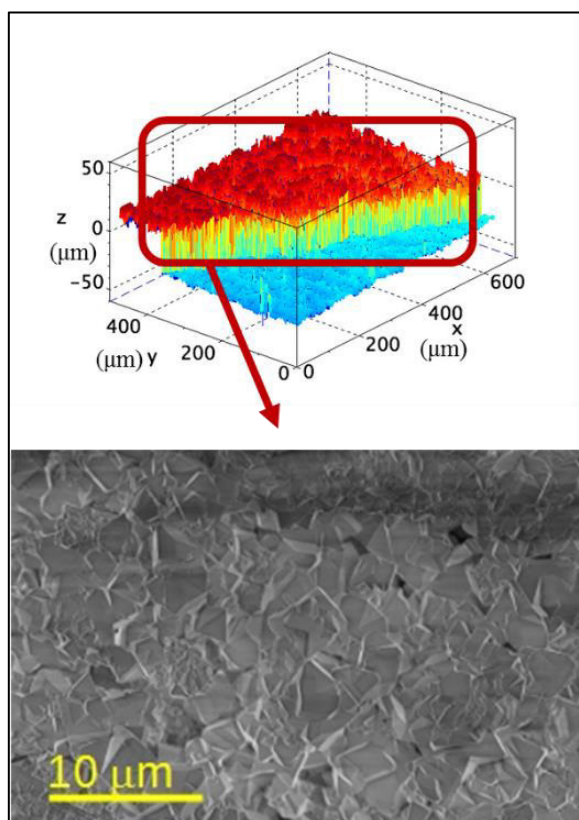


Fig. 6. CM (up) and FESEM (down) images of the original chloride patina.

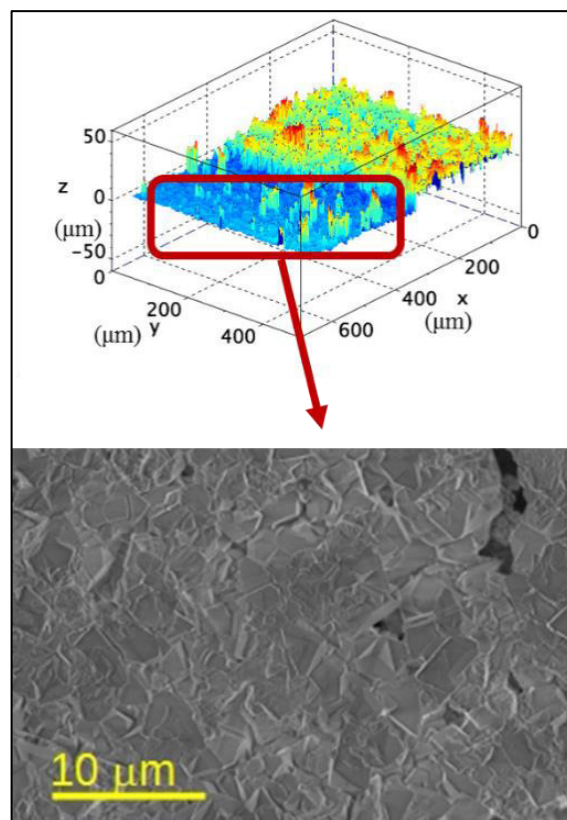


Fig. 7. CM (up) and FESEM (down) images of the 4 ns-laser treated chloride patina (laser cleaning A).

After the 4 ns cleaning treatment, the morphological investigations evidence a reduction of the patina thickness up to 10 μm even if FESEM images show that the morphology of the treated surface is partially unaltered: crystals are still present (Fig. 7).

In the case of the laser cleaning A on the chloride patina too, μXRD spectra evidence an increase in the relative intensity of the metallic copper peaks associated with a reduction of the copper chlorides peaks (Fig. 8).

Longer pulse duration treatments (8 ns, laser cleaning B) produced a different laser-material interaction on the simulated patinas, compared with the shorter pulse duration treatments (4 ns, laser cleaning A). As a matter of facts, the longer the pulse duration, the higher the penetration of the thermal effects and the deeper the penetration of the laser towards the surface.

This seems confirmed by the 8 ns treated area of the oxide patina: even if a change in the morphology is present, the patina thickness removed is not significantly different from the etching of the laser cleaning A.

CM images show a rougher surface at 8 ns treatment than at 4 ns treatment with a possible laser effect in melting the oxide patina associated with a possible re-solidification with a different texture of the etched materials (Fig. 9).

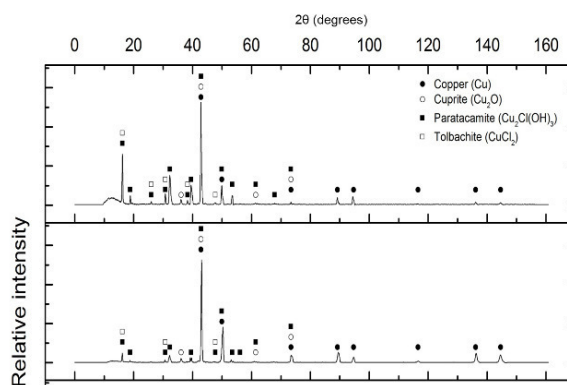


Fig. 8. μXRD spectra of the original (up) and 4 ns-laser treated area (down) chloride patina.

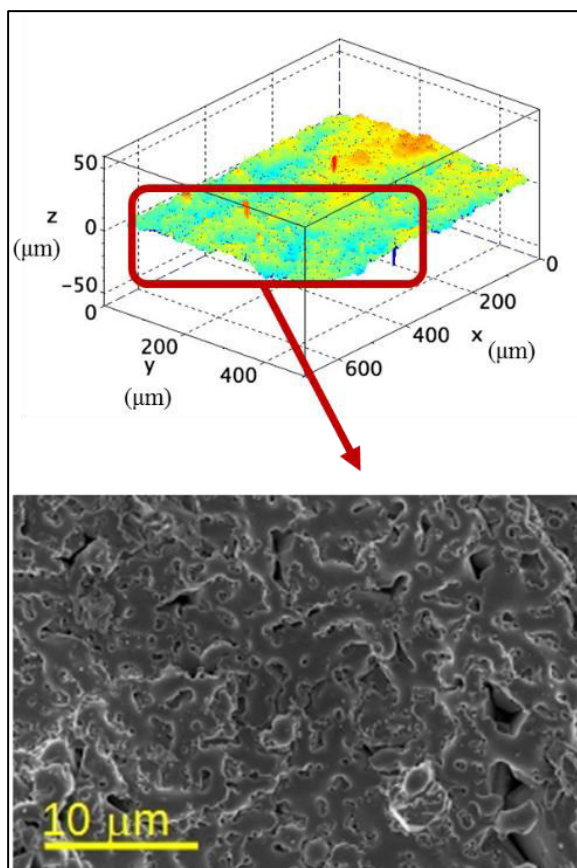


Fig. 9. CM (up) and FESEM (down) images of the 8 ns-laser treated oxide patina (laser cleaning B).

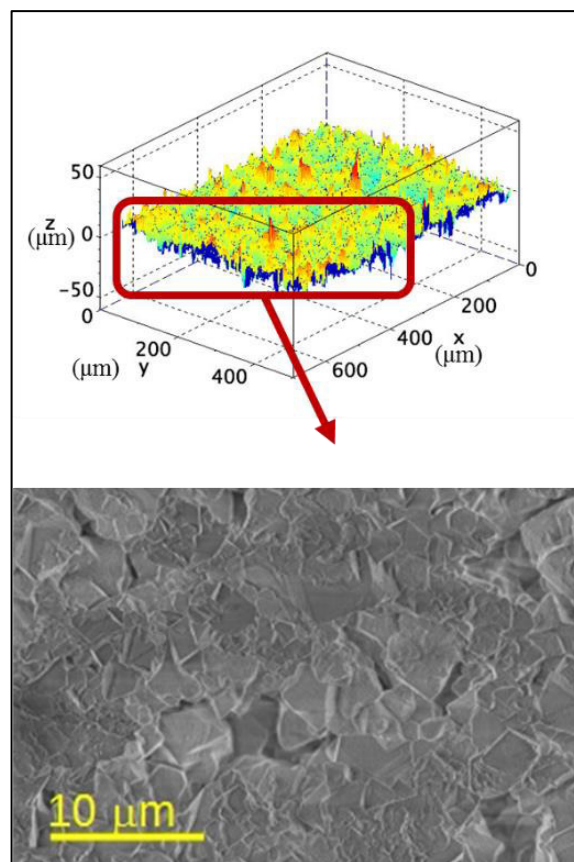


Fig. 10. CM (up) and FESEM (down) images of the 8 ns-laser treated chloride patina (laser cleaning B).

For the chloride patina, on the area submitted to laser cleaning B, CM and FESEM images show a reduction up to 5 μm in the patina thickness. In that case too, chloride crystals are still present after the cleaning treatments (Fig. 10).

For both artificial patinas, the similar XRD results are obtained on the areas submitted to laser cleaning A and B treatments: a slighter increase of the relative intensities of the metallic copper peaks is observed in both cases.

IV. CONCLUSIONS

In this preliminary study, a near-IR pulsed laser has been chosen in order to perform a low invasive and self-limiting laser cleaning treatment with the aim to remove only the dangerous corrosion products without affecting the original surface of metallic heritage artefacts.

The systematic research has been started carrying out tests with different laser pulse duration and power conditions on some copper reference specimens artificially patinated.

The experimental findings show that the laser coupled with the vector graphic editor is a powerful tool for performing precise and reproducible cleaning treatments. The pulse duration is an important parameter to be considered during laser cleaning procedures as it influences the interaction laser-materials.

The etching mechanism needs to be clarified as well as the possible laser effect in melting the patina, which could partially re-solidify on the surface with a different texture. Further investigations are going on in order to understand the etching mechanism and to analyse the influence of other laser parameters, such as overlapping, shorter laser pulses and laser wavelength.

V. ACKNOWLEDGEMENTS

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VI. REFERENCES

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