Analysis of selective laser cleaning of *patina* on bronze coins

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Abstract. The *patina*, is the result of a large number of chemical, electrochemical and physical processes which occur spontaneously during interaction of metal surfaces with the environment. In this work we want to analyze and remove the patina in artefacts, exposed to atmosphere for various decades. Here, experimental results about the laser cleaning of bronze coins by KrF (248 nm) and Nd:YAG (532 nm) lasers are reported. Both laser wavelengths were efficient to reduce the chlorine concentration on the surface of the coins more than 80 %, as demonstrated by Energy Dispersive X-Ray Fluorescence analyses.

1. Introduction

In the past the conservation of cultural heritage and in particular of metallic artefacts was considered a secondary problem either for the poor economic resources of countries or for the low technologic level to get restoration and conservation of art works without damage. Nowadays, the new technologic devices available in many laboratories have also increased the interest for the scientific applications in archaeological field. Particularly, since the seventies, due to technological progresses achieved in the field of power lasers and their great marketing and diffusion, new frontiers in the study of pulsed laser ablation have been opened [1-3]. Laser is applied in cultural heritage field, but its application is not so common. In 1997 a pulsed CO_2 laser was used to investigate samples of various metals showing that laser cleaning is efficient in removing organic paints and stains without damaging the bulk metal [4].

Recently, other pulsed lasers such as excimer lasers, Nd-Yag lasers, Er-Yag lasers, double frequency Nd-Yag lasers and triple frequency Nd-Yag lasers [5, 6], have been employed in the cleaning field too. It is well known in fact that pulsed laser beams, by choosing appropriate fluences, can induce a fast and controlled vaporisation of a few surface layers of the target. So this straightforward technique can reach meaningful results in the cleaning field reducing the risk of damage on artefact surface. As a whole, the laser cleaning is the result of many processes which depend on the irradiation conditions and artefact components.

In this work we focus our activity to study the laser cleaning of ancient bronze coins, undergone to corrosion. It is well known that a great variety of coins of metal or metallic alloys, under specific

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conditions, produce thin layers of corrosion products, called patina. Specific bronze patina present on outdoor exposed artefacts is the result of a large number of chemical, electrochemical and physical processes which occur spontaneously during interactions of metals with the environment.

In particular, bronze and copper alloys, exposed to urban atmospheres (with presence of CO, NO_2, SO, pollution, acid rains, …) for various decades, exhibit a greenish patina containing several compounds. Moreover, the artefacts, located in proximity of the sea, are in contact with marine aerosol which is constituted by small drops of seawater (mainly H_2O + NaCl). The chlorine reacts in the atmosphere with nitrogen oxide and forms hydrochloric acid as described by equation (1):

$$2\ NaCl + 3\ NO_2 + H_2O \rightarrow 2\ NaNO_3 + NO + 2\ HCl \quad (1)$$

The hydrochloric acid formation is the main responsible for a particular corrosion of bronzes called "*bronze's cancer*" [7]. This process induces the formation of copper chloride, which is soluble in water and forms copper (I) oxide (red cuprite) and hydrochloric acid as described by the equation (2) and (3), respectively:

$$4\ HCl + 4\ Cu + O_2 \rightarrow 4\ CuCl + 2\ H_2O \quad (2)$$

$$4\ CuCl + 2H_2O \rightarrow 2\ Cu_2O + 4\ HCl \quad (3)$$

Then, hydrochloric acid reacts again with the copper forming cyclic reactions which propagates the corrosion inside the coin. Besides, copper chloride hydroxides are formed in different, rarely solvable, allotropic forms delineated in the equation (4) and (5) and characterised by a blue-green pigmentation on the bronze surfaces.

$$2\ Cu + HCl + H_2O + O_2 \rightarrow Cu_2Cl(OH)_3\ \text{(atacamite)} \quad (4)$$

$$2\ Cu + HCl + H_2O + O_2 \rightarrow Cu_2Cl(OH)_3\ \text{(paratacamite)} \quad (5)$$

From the above chemical reactions it is possible to understand how the chlorine concentration is one of the main responsible of the deterioration of ancient bronze coins.

2. Experimental section

2.1. Theoretical basis

Lasers could be applied in the cultural heritage field, but it is indispensable to study carefully the process in order to determine the optimal conditions of irradiation: ablation of the patina and protection of the bulk. Depending on the the laser parameters, the photoablation can produce three kinds of photoinduced phenomena: photochemical processes (direct bond breaking and photodissociation), photothermal processes (heating by vaporation and heat conduction) and photomechanical processes (photoionization, plasma formation, fast expansion and shock wave propagation). Depending on the properties of the sample and on the irradiation conditions, such as wavelength and pulse duration, one of them may become dominant.

The heating region, produced by photothermal effects, depends on the duration of the laser pulse and on the thermal diffusion length, z_{th}, which is linked to the heat propagation by the following equation:

$$z_{th} \approx \sqrt{2D\tau} \quad (6)$$

where D is the heat diffusivity of the sample and τ is the laser pulse duration. Therefore, using short duration laser pulse, the heating propagation becomes short as well as the depth of the layer which could be ablated. The photomechanical effect is represented by the mechanical coupling coefficient, C_m, which is described by the equation (7) [8]:

$$C_m = \frac{P_a}{I} \quad (7)$$

where P_a is the ablation pressure (the explosion pressure produced by the shock wave provoked by the laser interaction) and I is the laser intensity. Moreover, photochemical effects are induced by UV laser photons. In effect, they have an energy near 5.0 eV, i.e. sufficient to produce chemical etching due to the break of the chemical bond Cu-Cl (that needs 3.76 eV at least), cleaning the bronze surface from Cl. Therefore, by the above considerations, it is difficult to determine *a priori* the optimal irradiation conditions in laser cleaning of coins exhibiting *patina* layers. So it is noteworthy to say that the region of laser cleaning can be controlled mainly by the laser wavelength, laser energy, pulse duration and target material.

In this work, preliminary results about the laser cleaning of bronze *patina* are reported by using two different nanosecond laser beams at UV and visible region. Both lasers operated at the same laser fluence just to observe how the choice of the wavelength can influence the cleaning process.

2.2. Instruments
We used two different pulsed lasers: a KrF excimer laser operating at 248 nm, 25 ns pulse duration and a Nd-Yag laser operating at 532 nm (second harmonic), 10 ns pulse duration. A 50 cm focal length lens was utilised to concentrate the laser energy on irradiating spot of 0.6 cm^2. A portable apparatus for Energy Dispersive X-Ray Fluorescence (EDXRF) analysis was used in order to evaluate the variation of the chlorine concentration before and after the treatment of laser cleaning. The characteristics of the EDXRF instrumentation is described in the references [9,10]

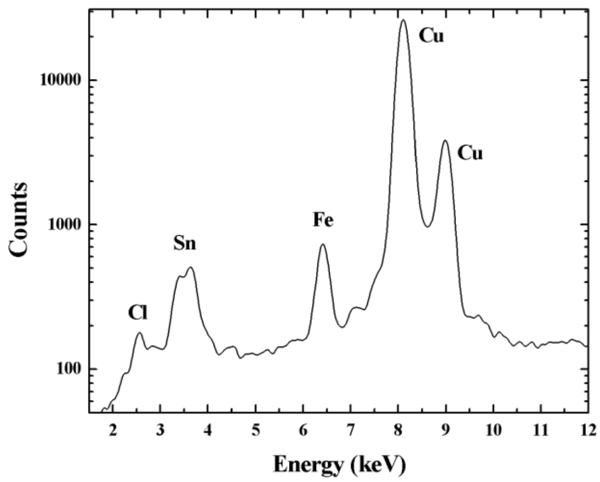

Figure 1. EDXRF spectrum before laser cleaning.

3. Results and discussion
Laser cleaning tests were carried on bronze coins made in Italy and aged at the first years of twentieth century. Sample surfaces presented a thin greenish alteration layer together with soil deposits. EDXRF analysis revealed that the corrosion layer was mainly due to chlorine (Fig. 1). Moreover, the characteristic X-ray L-lines of Sn, at 3.4 keV (Lα) and 3.7 keV (Lβ), and K-lines of Cu, at 8.04 keV (Kα) and 8.9 keV (Kβ), proved that the alloy constituting the coins was based on a Cu alloy containing Sn and Fe, i.e. it is a typical bronze.

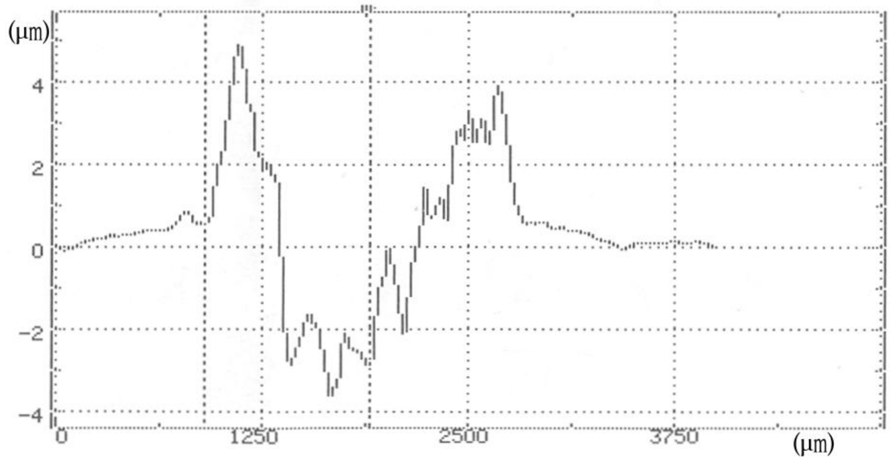

Figure 2. Typical result of the profiler.

In order to remove only the *patina* film without damages the coin surface, it was necessary to operate below the ablation threshold conditions related to bulk. They were determined experimentally as follows: utilizing a bronze sheet, with the same compositional characteristics of the coins (controlled by EDXRF analysis), having a flat area, we applied in different position at different laser pulse energies 50 laser shots. The laser spot was fixed at about 0.6 cm^2. "*Off line*" measurements of the ablated material were performed with a stylus surface profiler (Tencor Instruments ALPHA-STEP 200), in order to measure the crater profiles and to determine the ablation yield with different irradiance conditions.

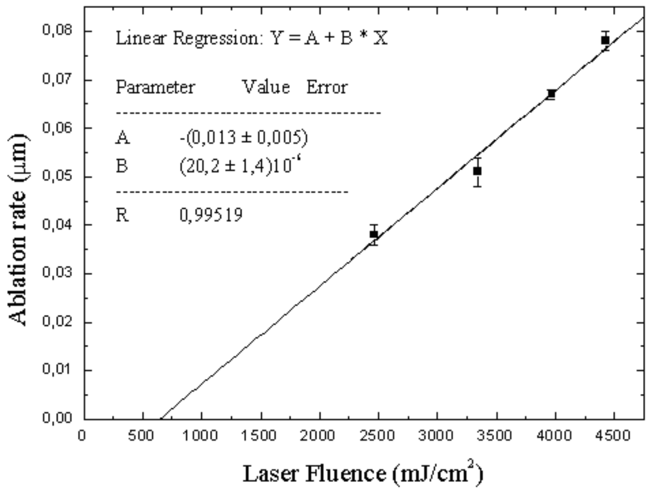

Figure 3. Etching rate of bronze sample as a function of the laser fluence.

Figure 2 shows a typical result of the profiler obtained by KrF laser for a total fluence of 3900 mJ/cm^2. At high laser fluences the spot exhibits enhanced edges. Fig. 3 shows the ablation rate as a function of the laser fluence for the KrF laser. Assuming that (the ablation rate is linearly dependent to the laser fluence) [12], the bronze threshold fluence was estimated of 655 mJ/cm^2 by the fit of the experimental data. This procedure was carried out also for visible laser obtaining a threshold fluence of 1000 mJ/cm^2. Therefore, the values of the fluence to operate laser cleaning were fixed at 300 mJ/cm^2 and 500 mJ/cm^2 per single pulse for KrF and visible laser respectively. The laser spot was about 0.6 cm^2. In order to ablate the entire surface, the coin has been shifted horizontally and vertically with respect to the laser beam.

Figure 4 shows the EDXRF spectrum, in the low X-ray energy region, before and after the cleaning treatment by KrF laser. The characteristic X-ray K-lines of Cl at 2.6 keV (Kα) and 2.8 keV (Kβ) and L-lines of Sn at 3.4 keV (Lα) and 3.7 keV (Lβ), useful for this investigation, have intensities proportional to the elements concentration in the analyzed surface. The proportionality takes in consideration the X-ray production cross section and the detection efficiency of the detector.

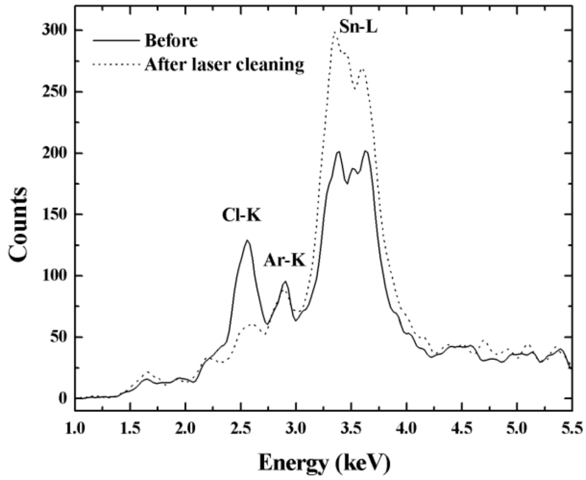

Figure 4. EDXRF spectrum before and after UV laser cleaning.

After 30 laser shots, with a repetition rate of 1Hz, the chlorine concentration decreases from 2.6 % w/w to a value below 0.5 % w/w (detection limit) against the increasing signal of tin due to its surface emersion. The analysis was repeated on several samples, and it has shown similar results. This confirms that the technique is reproducible.

These results confirm that the laser cleaning is able to remove safely the *patina* film, i.e. corrosion products of the coin surface without damaging the coin matrix.

In Fig.5 the area of a bronze coin irradiated by UV laser is showed. it is evident how the green colour of the patina disappears. The figure shows the bronze coin during the ablation process which subsequently affected the whole coin.

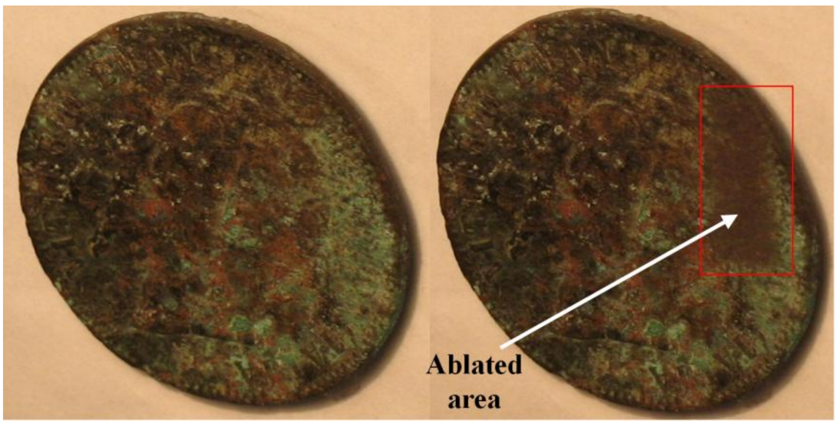

Figure 5. Photo of a virgin (left) and a processed coin (right).

Studies performed by using visible laser gave also good results on the removing of chlorine concentration from the surface of bronze coins (Fig. 6). In fact, after 30 laser shots, the chlorine concentration decreases from 2.8 % w/w to a value below 0.5 % w/w (detection limit). The decreasing of tin signal reveals that visible laser cleaning is not selective because the removal of *patina* is accompanied by a reduction of tin.

Moreover an interesting observation was derived by comparing the irradiated areas at the two wavelengths. It was possible to observe a colour changing of the coin surface. The coin cleaned by KrF laser exhibited a remarkable darkening. Same change was not observed for the visible laser treatment: in this case the ablated areas appeared very bright and polished [11].

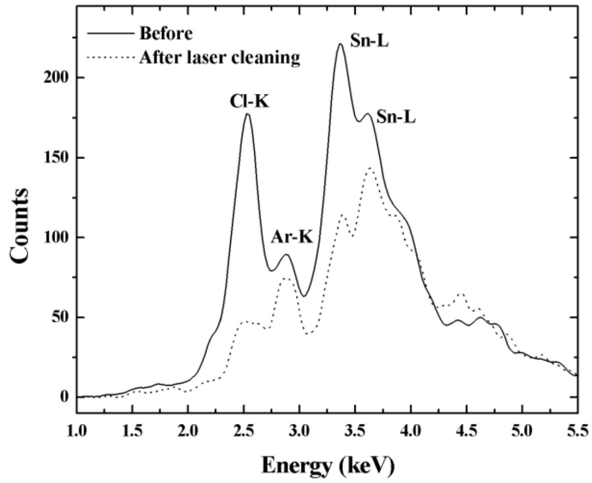

Figure 6. EDXRF spectrum before and after visible laser cleaning.

4. Conclusions

Experimental results about the laser cleaning of bronze coins show that the pulsed lasers can be used safety as a powerful tool to remove the *patina* of bronze coins. Operating below the threshold laser fluence, the UV and visible laser actions are able to remove the greenish patina from the surface of the coins more than 80 %. Besides, the obtained results prove that UV laser cleaning is able to preserve the bulk of the coin while that is not true for visible laser cleaning.

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