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Laser cleaning on Roman coins

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ABSTRACT Ancient metal objects react with moisture and environmental chemicals to form various corrosion products. Because of the unique character and high value of such objects, any cleaning procedure should guarantee minimum destructiveness. The most common treatment used is mechanical stripping, in which it is difficult to avoid surface damage when employed. Lasers are currently being tested for a wide range of conservation applications. Since they are highly controllable and can be selectively applied, lasers can be used to achieve more effective and safer cleaning of archaeological artifacts and protect their surface details. The basic criterion that motivated us to use lasers to clean Roman coins was the requirement of pulsed emission, in order to minimize heat-induced damages. In fact, the laser interaction with the coins has to be short enough, to produce a fast removal of the encrustation, avoiding heat conduction into the substrate. The cleaning effects of three lasers operating at different wavelengths, namely a TEA CO_2 laser emitting at $10.6\,\mu m$, an Er : YAG laser at $2.94\,\mu m$, and a 2ω-Nd : YAG laser at 532 nm have been compared on corroded Romans coins and various atomic and nuclear techniques have also been applied to evaluate the efficiency of the applied procedure.

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1 Introduction

Ancient metals, especially copper alloys, have been studied in the past on a regular basis, with emphasis on the surface modifications they have suffered in the course of time [1]. Metal artifacts that have been buried underground or exposed to the atmosphere undergo corrosion, which critically depends on the environment and can eventually destroy them [2]. Such samples show a variety of damage with the most common being superficial formations and encrustation forming a brittle surface layer. In most of the cases the surface is covered by green calcareous accretions (malachite) including silicates that completely overlay the oxidation patina (typically cuprite) [3].

Careful use of suitable conservation treatments is therefore necessary to preserve the material and the valuable scientific information that the artifacts carry. Cleaning is usually the first difficult step of conservation operations undertaken when preserving metal artifacts. Any cleaning must be carried out with great respect and consideration for the original object's form, function, and chemical composition. The most common treatment is mechanical stripping, but it is difficult to avoid some surface damage with traditional mechanical methods, since they are difficult to control and have poor precision [4].

Lasers are currently being tested for a wide range of conservation duties. As they are highly controllable and can be selectively applied, lasers can be used to achieve more effective and safer cleaning of archaeological artifacts. Lasers offer high ablation control with a very precise spatial targeting and high selectivity, and they are also safer for the user. They have been used on various materials such as copper, bronze, steel, lead, and brass with very promising results. However, application of laser cleaning on metal artifacts is limited for the time being [4]. For this type of application, different materials may require a laser pulse width ranging from nanoseconds to microseconds, in order to optimize the cleaning results. Laser cleaning occurs by a combination of mechanisms, the relative importance of each depends on the fluence (energy density) used and the properties of the inorganic encrustation and corrosion products of metals. Since most metals absorb strongly in the visible, while possible organic compounds on the surface absorb in the far infrared, cleaning, at least in the visible spectrum, is usually carried out at relatively low fluences to minimize any risk of damage to the substrate [3, 4]. Strong absorption of energy leads to rapid heating and subsequent expansion of the dirt or the corroded particles.

The basic criterion that led us to choose laser techniques to clean Roman coins was the requirement of pulsed emission, in order to produce a fast removal of the encrustation while avoiding heat conduction into the substrate. Therefore, we employed only lasers with pulse durations shorter than $100\,\mu s$ [3] and thus, although the expansion happens quickly, the resultant forces are sufficient to eject corroded particles from the surface.

For controlling and evaluating the cleaning procedure, various analytical optical, X-ray (energy dispersive X-ray fluorescence – EDXRF), and ion beam techniques (Rutherford back-scattering – RBS and nuclear reaction analysis - NRA) have been employed. EDXRF is a well-established technique for non-destructive compositional analysis of homogeneous

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metal alloys, but it is also widely accepted that due to its limited depth resolution, it is inherently unreliable for compositional studies of ancient metal artifacts with a corroded surface [5]. However, by adopting a suitable strategy for interpreting EDXRF data, elements that have been enriched or depleted from the surface can be identified and the effectiveness of the cleaning procedure can be evaluated with respect to the degree of removal of certain corrosion products [6, 7].

2 Experimental methods

Determination of the optimum laser-cleaning parameters (wavelength, energy density, pulse duration, repetition rate, and the number of applied pulses) is closely dependant on the composition of the encrustation material and the substrate as well as the encrustation's thickness and its relative relationship to the substrate. This paper presents initial experimental measurements taken in an effort to further evaluate the laser cleaning process, while keeping the parameter of the laser fluence constant during the irradiation processes. Two Roman coins were investigated having an average thickness of 1.2 mm and diameters of 20 mm and 18.5 mm. Three laser systems were used for the ablation: a Q-switched 532 nm 2ω-Nd : YAG laser, a free-running Er : YAG 2.94 μm laser, and a 10.6 μm TEA CO$_2$ laser. Their typical pulse durations were of 8 ns, 80 μs, and 80 ns, with a maximum repetition rate of 10 Hz, 1 Hz, and 1–5 Hz. Their beam divergences were 0.6 mR, 0.7 mR, and 5 mR respectively. All lasers operated at a fluence of 0.4 J cm^{-2}.

To determine the most suitable irradiation conditions, very careful examination by optical microscopy, EDXRF, RBS, and NRA have been carried out during the cleaning treatment.

A portable XRF unit consisting of a thermoelectrically cooled PIN X-ray detector having a 200 eV resolution at Mn K_α, and a Rh-anode side-window X-ray tube of 50 Watt power, with a 125 μm Be window were used for the measurements. Two operating conditions were selected for optimizing the excitation conditions. In the case of the 40 kV filtered excitation, a broadband excitation is achieved and elements with atomic numbers in the range $Z = 16$–92 can be detected. An additional EDXRF measurement was performed at 15 kV in order to achieve selective excitation of the low energy characteristic X-ray lines that can provide more useful information about the superficial corrosion layers structure with respect to the former excitation condition. The irradiated area was restricted by proper collimation to about 3–4 mm^2.

Two ion beam analytical techniques, RBS and NRA have been used for the study of either the surface structure of the coins or for the detection of carbon via the ^{12}C (d,p) reaction. For the RBS measurements a deuteron beam was used having a 1 nA current, whereas for the carbon detection in the NRA via the ^{12}C (d,p) reaction an energy of $E_d = 1.3$ MeV was used. The amount of carbon deposited on the surface of the treated coins is essential for evaluating the applied cleaning procedure.

3 Results

3.1 Cleaning procedure

During the cleaning procedure, optical microscopy photographs were taken in reflected light mode to control the microstructure and texture of the coins surface [8]. Bulk erosion, spikes, flakes, and micro pores were present on the surface, making the controlled removal of the rust from the bulk surface during IR and mid-IR ablation more difficult. Although the three laser systems employed are inducing different removal mechanisms, the laser fluence was kept constant in order to reduce the many variables of the experiment. The tests were carried out using different laser sources, and useful indications of the lasers suitability were deduced.

From the approximation of the thermal conduction equation at a given laser fluence, short pulses are expected to induce a higher temperature rise with respect to long ones [9]. The boiling temperature of the copper alloy limits the energy fluence to low values. Several energy fluences were used but by choosing a fluence of ~ 0.4 J/cm^2, for all different laser spot sizes, it was also possible to control the laser ablation process more efficiently [3, 4, 10, 11]. At higher fluences the removal mechanisms became more complex involving the formation of plasma just above the surface and discoloration of the surface occurred. On the contrary at lower energies it was almost impossible to clean the corrosion products from the surface .

As for the pulse width, material removal by nanosecond laser pulses can be generated by pressure confinement, or by spallation, while above the vaporization threshold, ablation can occur by fast thermal explosion. In the nanosecond range, plasma mediated ablation is usually characterized by a strong recoil stress release to the target [12]. Apart from a significant role in the ablation dynamics, the plasma formation can reduce control of the ablation rate and generate mechanical side effects. On the other hand, when the pulse width is in the range
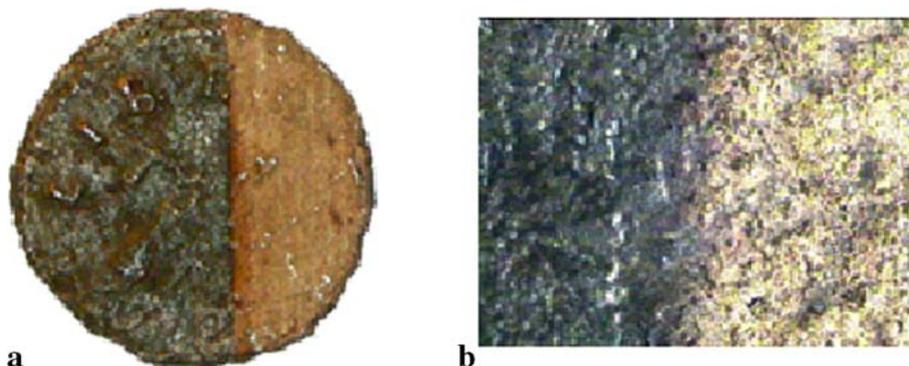
FIGURE 1 **a** Laser cleaned Roman coin with both Q-switched 2ω-Nd : YAG laser (*right side*) and a TEA CO$_2$ laser (*left side*) **b** Microscopic (40x) photo of the surface morphology

FIGURE 2   **a** Laser cleaned Roman coin with both Q-switched 2ω-Nd : YAG laser (*right side*) and a TEA CO_2 laser (*left side*) **b** Microscopic (40x) photo of the surface morphology

of microseconds, the mechanical effects are much lower and sometimes negligible [13].

In the Figs. 1 and 2, the ablated Roman coins are shown, exhibiting a different texture. First of all, at a constant repetition rate we noticed a different ablation response for the two coins, especially when the 532 nm-laser was used. The ablation of the first coin in one to four successive steps by the Q-switched Nd : YAG laser, had driven a rapid expansion, structural weakening, and micro fragmentation of the corrosion products, and finally resulted in a rather smooth cleaning with a bright surface color (Fig. 1a and b right side). On the contrary, the cleaning of this coin by the CO_2 laser resulted in a rather smooth but darkened area (Fig. 1a and b left side). The reaction of the second coin, shown in Fig. 2a and b, was totally different. Large amounts of spalling and black color corrosion surface were noticed, resulting in a less satisfactory cleaning of the surface. Additionally, during the CO_2 cleaning, a plasma formation was noticed and an orange glow during laser shooting was observed. Furthermore, the Er : YAG, 2.94 μm laser, was tested for cleaning, but similar light and dark areas appeared on both coins like those produced by the CO_2, 10.6 μm laser. Therefore, most of the subsequent IR ablations were carried out only with the CO_2, 10.6 μm laser and only a few experiments were attempted with the Er : YAG laser on moisture containing coins.

3.2   *Analytical results*

EDXRF analysis of the two Roman copper coins provided: 1) elemental concentrations of the alloys major, minor, or trace elements and 2) evaluation on a semi-quantitative basis of the lasers cleaning efficiency through the measurement of compositional changes of the elements present in a near surface layer.

The compositional data was obtained using the 40 kV excitation voltage on the XRF unit. The X-rays were applied on a careful and time consuming laser cleaning procedure that revealed the original surface of the coins. The XRF results can be considered as very reliable, even when the two coin surfaces exhibited various irregularities, or if minor corrosion products were still present on the cleaned surfaces. It has been shown that surface relief's affect the elemental concentrations [14] more or less to the same extent. This is also true if we consider the presence on the analyzed cleaned areas of minor amounts of light elements (carbon, oxygen) non detectable by XRF. Therefore, any influence of the aforementioned factors on the measured concentrations is cancelled out

through the normalization procedure and the results can be interpreted as representative of the core composition of the coins. More specifically, the two coins are two different Cu-Sn-Pb-Ag alloys with corresponding concentrations, for coin 1 of Cu: 86.8%, Sn: 7.4%, Ag: 1.6%, and Pb: 4.2% and for coin 2: Cu: 97.5%, - Sn: 1%, Ag: 0.56%, and Pb: 0.94%.

In order to study now the compositional changes of Cu and Sn during the cleaning procedure, different approaches were used. It is useful at this point to note that for the cleaned area of coin 1 the XRF information depth is 24 μm [7] (95% intensity) using 40 kV voltage for Cu K_α, whereas it is 11 μm (95% intensity) for the 15 kV. These depths are increased by a factor of three, if oxygen substitutes 50% of the alloy matrix.

For Cu, the ratio of its intensity at 15 kV to 40 kV is a rough indication of the surface content. Therefore, by considering this ratio it was observed that cleaning of the two coins by both lasers increases almost to the same degree (almost 20%) the "upper" surface layer copper content. A plausible explanation for this increase could be that due to the cleaning procedure there is a reduction of the corrosion products where copper has a lower concentration with respect to the bulk.

With regard to the behavior of Sn during the cleaning procedure, the Sn-*L* characteristic X-rays, exhibiting small information depth (3.3 μm in our example for 95% intensity), can be used to monitor its compositional changes from the surface studied. From Fig. 3 we can observe that for coin 1, a surface enrichment of Sn exists and both lasers remove about 30% of
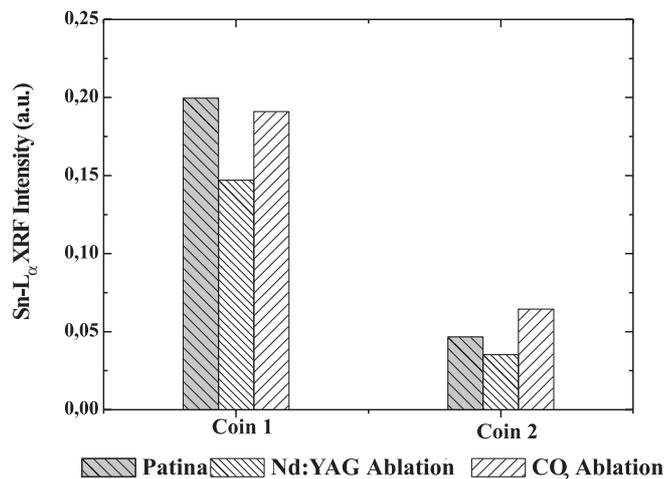
FIGURE 3   The intensity of the fluorescent Sn L_α X-ray line, measured at 15 kV in the patina and treated surfaces of the two coins by both lasers
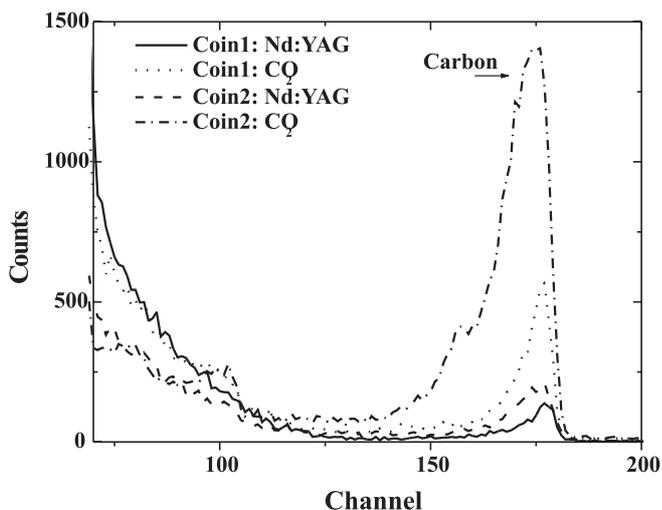
FIGURE 4 Energy spectrum produced via the ^{12}C (d,p) nuclear reaction at the deuteron energy $E_d = 1.3$ MeV

Sn contained in the patina. In contrast, significant changes are not observed in the case of coin 2, most likely indicating that either Sn-enrichment was not important, or that the cleaning procedure using both lasers was not successful for the removal of its corrosion products.

The RBS spectra of the cleaned areas of both coins provided only comparative information, since the roughness of the analyzed surfaces (estimated to be a few microns) and the gradient of the elemental concentration towards the bulk, does not allow any precise simulation of the spectra. However, the treated surfaces of coin 1 and coin 2 by the Nd : YAG laser were found to be in relatively better condition with respect to the treatment by CO_2 laser. In particular, the surface of coin 2 treated by CO_2 laser (Fig. 2b, left side) showed a significant presence of carbon and oxygen on the surface. For this reason NRA was also used in order to evaluate the carbon content on the treated areas of both coins. From Fig. 4 we can observe that on the two areas treated by the CO_2 laser, a significant amount of carbon was deposited, in a rather thick surface layer (a few microns thick). On the other hand the areas treated by the Nd : YAG laser showed a significant decrease of carbon content (by a factor of 4 for coin 1 and by a factor of 7 for coin 2). The presence of carbon can also be revealed from the EDXRF spectra, at 15 kV excitation voltage, if we compare the intensity of the Rh-L scattered X-ray line that originates from a surface layer up to 2 microns. The amount of scattering crucially depends on the low atomic number elements of the surface layer and increases considerably in the cleaned areas when the CO_2 laser is used.

3.3 Discussion

A knowledge of the compound properties such as thermal conductivity, optical reflectivity, and thermal expansion coefficient, can be used to predict details of the laser cleaning to be applied to a specific corrosion-bulk layer system, without damaging the bulk. The threshold fluence depends on the square root of the thermal conductivity and consequently differs from one material to another and affects the laser cleaning process [15]. The difference of thermal conduc-

tivity between the substrate and the corrosion layer affects the laser threshold fluence [15]. If the bulk material has a higher thermal conductivity, as compared to the corrosion products on it, it requires more pulses (longer treatment) to be cleaned, because the transmitted energy easily diffuses into the substrate and the energy accumulated in the corrosion film cannot reach the threshold energy for ablation. The thermal diffusion length, which characterizes the ablation depth, is reduced with lower thermal conductivity and the material removal is more confined on the corrosion surface especially for small pulse durations [9, 16, 17]. The presence of higher Sn concentration at the surface layer of the first coin seems to help the cleaning process by both lasers, since the Sn thermal conductivity is lower than that of Cu [15, 18, 19]. For the second coin, the remaining surface, as well as various microscopic explosion debris, may be the result of the laser beam scattering on the near-surface plasma, and of the plasma action on the encrustation.

As for the cleaning efficiency of the two lasers, it seems from the Figs. 1b and 2b that the Nd : YAG more efficiently removed the corrosion products from both coins, although in the second coin the treated area was darkened (Fig. 2b, right side). The pulse width and the laser wavelength, may be significant in explaining the different behavior. Literature reports state that the thermal conductivity of Cu, Ag, Pb, and Sn increases with the pulse width, and this explains the better behavior of the 8 ns laser pulse (Nd : YAG) with respect to the 80 ns one [16]. The 8 ns laser pulse leads to a rapid energy absorption, but in a very thin layer, which is instantaneously evaporated and removed, preventing conduction of heat to the underlying bulk material [9, 17]. It should be stressed that selective cleaning requires that the surface layers of the samples display higher absorption coefficient as compared to the substrate. Overall the short duration laser wavelength of 532 nm (Nd : YAG) seems to be more appropriate, for an efficient cleaning process based primarily on a photomechanical rather than a thermal process, when the samples were kept dry.

4 Conclusions

The cleaning effects of the TEA CO_2, 10.6 μm (80 ns), the free-running Er : YAG, 2.94 μm (80 ns), and the Nd : YAG, 532 nm (8 ns) lasers on Roman coins were investigated. The 2ω-Nd : YAG laser produced better results in general,, when the samples were dry. Some additional experiments with wet samples gave improved cleaning performance with all three lasers. Furthermore, additional experiments with both a Q-switched Er : YAG (190 ns), and a free running Er : YAG (80 μs) on wet coins, led to an enhanced cleaning effect, with the Q-switched Er : YAG being more efficient, which is in reasonable agreement with [20].

The exact knowledge of the physical and chemical properties of materials to be treated is critical when choosing a laser suitable for surface cleaning prior to conservation. Many other factors, such as the presence of spikes, flakes, and micropores on the surface, or the plasma formed during laser cleaning, which absorbs most of the energy in the laser pulse, affect the cleaning efficiency. Even the same laser gives different results depending on the character of the bulk substrate. X-ray and ion beam techniques seem to be useful for a qualitative

evaluation of the cleaning efficiency and to highlight specific problems or possibilities of the laser treatment. More detailed research is under progress, involving SEM-EDX and XRD diagnostic techniques, and once the laser technique is fully understood, more precious registered archaeological artifacts will also be treated.

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