LASER CLEANING OF CU-BASED COINS

E. D'Anna[1] , M.L. De Giorgi[1], A. Lorusso[1], A. Perrone[1], A. Della Patria [2] and H. De Rosa [3]

[1]Physics Department, University of Salento, Italy

[2]Art Diagnostic Group, Arnesano (LE), Italy

[3]Departamento de Ingenieria Mecanica, Universidad de Buenos Aires, Argentina

Laser cleaning technique has been using as a versatile tool for the restoration treatments of archeological artifacts [1]. This technique is, indeed, powerful for removing contaminated layers with a very precise spatial targeting and high selectivity. Nevertheless, before any laser cleaning procedure and for each specific material, a dedicated study is mandatory to find the most suitable irradiation conditions to preserve the original characteristics of the artifact. In particular, for metal artworks the choice of laser wavelength, pulse duration and fluence is very important in order to avoid heating and the consequent melting and damage of the original surface [2]. Laser cleaning was tested on Argentinean coins, made of Cu alloys and found in an urban archaeological site of Buenos Aires named Corralon de Foresta. The metal artifacts have been buried for a long time and covered by cinders of an urban waste used in the XIX century to embank the Moldonado river. In this work, as a case study, results concerning the laser cleaning on a bronze coin (Fig.1) identified as 1 Centavo and realized in 1884 are reported. By the naked eye, a quite homogeneous dark patina with the presence of some localized greenish corrosions were evident in the surface. A Q-switched Nd:YAG laser

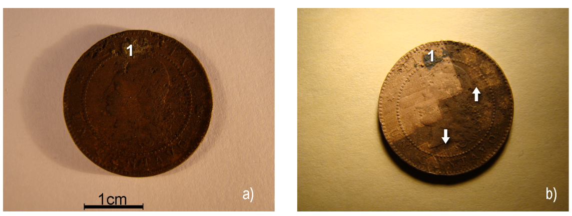

Figure 1. The Argentinean coin a) before and b) after laser cleaning treatments.

was used, being IR radiation the most proper in cleaning bronze artifacts. The laser beam was shaped by a square aperture to obtain a uniform laser spot area of 2x2 mm^2. The coin was fixed on a motorized and computerized x-y raster system. In order to make sure that all parts of the coin surface were exposed homogeneously to the laser beam, the raster paths of the laser cleaning procedure were chosen in such way that consecutive laser shots partially superimposed, with overlapped slices width less than 0.1 mm. Pre-cleaning scanning electron microscopy associated with energy dispersive analyses (SEM/EDX) and micro-Raman microscopy investigations provided information concerning the Cu alloy and the corrosion products of dark patina. As inferred from SEM/EDX measurements, the coin was made of a typical binary bronze alloy of Cu and Sn; significant concentrations of O, C, Si, Na were detected, too, as well as traces of Fe, Ca, Cl and S, coming from the burial outermost layers. Micro-Raman analyses, performed in different areas on the coin surface, gave the typical spectra of cuprite and malachite, as well as feldspar, spinel, silica and iron oxide (hematite) (Fig.2a). Sulphur found by

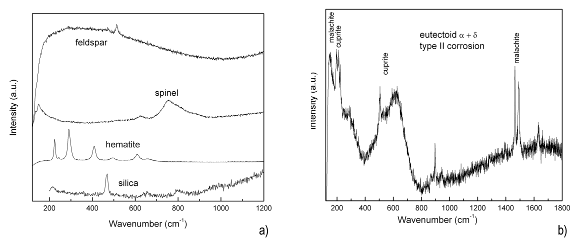

Figure 2. Typical micro-Raman spectra of the coin: a) before laser irradiations in four different areas and b) after laser irradiations.

SEM/EDX analyses could be due to copper sulphides (CuS, Cu_2S) or sulphates ($CuSO_4$), even if no Raman signal has been detected. In order to avoid heating damage of the artifact, preliminary irradiation tests were performed on some Cu-alloy samples with a similar composition of the coin made of Cu and Sn (3.5 % wt). The laser damage threshold at 1064 nm was empirically estimated at about 2 J/cm^2. During the preliminary tests (shown in Fig.1b by arrows), laser parameters were systematically changed to find the best operating procedure. The laser cleaning action was then performed by fixing the laser fluence at 1 J/cm^2, below the damage threshold, and changing the coin position after each pulse. During the irradiations the artifact was maintained dry, since it was observed that, fixed the fluence and the pulse number, the cleaning efficiency was not improved by wetting the surface with water. After laser treatments it was observed, by the naked eye, that the dark overlayer was successfully removed and the original details were more appreciable (Fig. 1b). Anyway, the laser cleaning was not efficient in restoring the original surface in the greenish area, labelled in the figure with the number 1, where the corrosion was deeper into the coin. After the laser irradiation the area changed its colour from green to dark grey. By SEM micrographs, it resulted that the morphology of the treated areas did not change as effect of the laser irradiation and EDX analyses showed that the laser cleaning was efficient in reducing drastically the burial contaminant elements (Si, Na, Fe, Ca, Cl and S) on the coin surface. Moreover, micro-Raman spectra showed the eutectoid with the preferential corrosion of the type II phase [3], characterized by the simultaneous presence of malachite and cuprite (see Fig. 2b). In the area indicated by (1), besides malachite and cuprite, the dark area included carbon as well. As conclusion, the main outcome of laser treatments on the 1 Centavo coin was the removal of the dark patina, without affecting surface morphology and ensuring good visibility of the details, even if the surface cuprite/malachite corrosion still remains. Nevertheless, laser action, in our experimental conditions, was not able to eliminate the greenish accretion.

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