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Evaluation of laser cleaning for the restoration of tarnished silver artifacts

T. Palomar[a,b,*], M. Oujja[c], I. Llorente[a], B. Ramírez Barat[a], M.V. Cañamares[d], E. Cano[a], M. Castillejo[c]

[a] Centro Nacional de Investigaciones Metalúrgicas (CENIM-CSIC), Avda. Gregorio del Amo 8, 28040 Madrid, Spain
[b] Depto. de Conservação e Restauro and Research Unit VICARTE-Vidro e Cerâmica para as Artes, Campus de Caparica, FCT-UNL, Quinta da Torre, 2829-516 Caparica, Portugal
[c] Instituto de Química Física Rocasolano (IQFR-CSIC), Serrano 119, 28006 Madrid, Spain
[d] Instituto de Estructura de la Materia (IEM-CSIC), Serrano 121, 28006 Madrid, Spain

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ABSTRACT

In this study we evaluate the laser cleaning of tarnished pure and sterling silver substrates using a nanosecond Q-switched Nd:YAG laser at 1064, 532 and 266 nm. To assess the effects associated with cyclic laser cleaning treatments, several cycles of tarnishing followed by laser cleaning were applied on silver coupons that were characterized by gravimetry, colorimetry, scanning electron microscopy, X-ray photoelectron spectroscopy and micro-Raman spectroscopy. According to the obtained results, none of the three wavelengths is recommended for laser cleaning of pure silver objects, while for sterling silver artifacts, the visible laser wavelength of 532 nm seems the most appropriate.

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1. Introduction

Historical artifacts located in museums and private collections are exposed to different atmospheres (exhibition halls, showcases, storage, packaging, etc.) which can contain various degradation agents that threaten their preservation. For metallic objects, corrosion is the main degradation phenomenon, caused by reaction of the metal with environmental humidity and pollutants, such as SO_2, NO_x, O_3, reduced sulfur compounds (H_2S, OCS) and volatile organic compounds (VOC) [1–3].

Tarnishing (the formation of a thin colored corrosion layer) is the most common alteration mechanism of silver objects. It is produced by reduced sulfur gases, principally H_2S, and other organic molecules from atmospheric pollution, such as carbonyl sulfide (OCS) and dimethyldisulfide ($(CH_3)_2S_2$) [4–8]. Tarnishing is originated in the first stage by the reaction of the environmental oxygen with the silver surface forming a thin oxide film. Then, the presence of reduced sulfur species in the atmosphere can displace these oxides leading to the formation of silver sulfide (Ag_2S). Humidity, NO_2, ozone and ultraviolet radiation can act as accelerators of the process [7,9]. Relevant chemical reactions involved in the tarnishing mechanism are:

$$2Ag + H_2S + ½O_2 \rightarrow Ag_2S + H_2O \quad (1)$$

$$2Ag + OCS \rightarrow Ag_2S + CO \quad (2)$$

Ag_2S is a black compound and its formation on the silver surface produces a loss of the shine and a change of color to a dark appearance, what is unacceptable for an historic artifact [7]. Restoration treatments are applied to clean tarnished silver objects and to recover their original shiny metallic appearance. The cleaning procedures most frequently applied on historical silver objects are of mechanical, chemical and electrochemical nature [7]. Mechanical methods, mainly applied by using hand tools and abrasives, are the most frequent cleaning procedures, nevertheless they produce localized and uncontrolled mass loss leading to a fast re-tarnishing process [10–12]. Chemical cleaning methods are less frequently used, although commercial products or thiourea acid solutions have been employed due to their fast cleaning effects. Thiourea acts as a fast chelating agent dissolving the tarnish layer. However this effect is not easily controlled and usually leave a completely het-

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[*] Corresponding author at: Centro Nacional de Investigaciones Metalúrgicas (CENIM-CSIC), Avda. Gregorio del Amo 8, 28040 Madrid, Spain.
E-mail address: t.palomar@csic.es (T. Palomar).

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erogeneous surface which could retain residues from the cleaning solution [12,13].

Recently, lasers have been used for the removal of different corrosion layers, encrustations, and coatings on archaeological and historical metal objects [14–25]. The application of lasers in conservation faces the challenge to deal with some issues, among others the preservation of the original surface and the formation of unwanted laser induced alteration layers [26,27]. Most of the previous studies have been focused on the laser irradiation effects, using different wavelengths and pulse duration, on the corrosion layer and on the underlying material after a single laser treatment [28–34]. However, the effects associated with successive laser cleaning treatments on tarnished silver objects have not been addressed before. Real artifacts in museums and collections are repeatedly subjected to these cycles of natural tarnishing and cleaning treatments, so the study of the cumulative effect of any treatment is highly relevant for the long term preservation of these heritage substrates.

The aim of this study is to evaluate the effect of laser irradiation using nanosecond pulses of three different wavelengths at 1064, 532 and 266 nm on artificially tarnished pure and sterling silver coupons with the objective of determining the optimal laser conditions for the removal of the tarnish layers in a controlled manner and with the minimum damage to the underlying silver substrates. Sterling silver was studied as representative of a typical alloy used in historical silver objects. The most important aspect of the work presented here involves the evaluation of laser cleaning effects associated with cyclic tarnishing-laser cleaning treatments, by applying different cycles of artificial tarnishing followed by laser cleaning of the considered samples. As mentioned, the literature concerning this issue is quite scarce or non-existent. The laser-induced physical and chemical modifications on tarnished silver substrates were assessed using different techniques. Surface morphology and color variations were evaluated using scanning electron microscopy (SEM) and colorimetry, and chemical composition using micro-Raman spectroscopy and X-ray photoelectron spectroscopy (XPS).

2. Experimental

2.1. Samples

Coupons ($2.0 \times 1.0 \times 0.1\,cm^3$) of pure silver (99.50 wt% of silver, 0.30 wt% of iron, 0.13 wt% of chromium, 430 ppm of copper, 216 ppm of sulfur) and sterling silver (92.47 wt% of silver, 7.28 wt% of copper, 0.26 wt% of palladium), purchased from SEMPSA JP, were used as substrates. Their composition was analyzed by wavelength dispersive X-ray fluorescence (WDXRF) with a Bruker S8 Tiger system. The samples were abraded with emery paper, down to grade 2000, and washed with ethanol in an ultrasonic bath for five minutes. Tarnishing was carried out by exposure of the coupons for 72 h to a sulfur vapor environment according to the thioacetamide corrosion test (TAA Test) at 22 °C [35]. The tarnish layer over the silver and sterling silver coupons presented a thickness up to 300 nm according to measurements carried out using SEM in cross-section preparations.

2.2. Laser irradiation

Laser cleaning tests were performed with a Q-switched (QS) Nd:YAG laser system (Quantel Brilliant B) that delivers pulses, at the fundamental wavelength of 1064 nm and its second and fourth harmonics at 532 and 266 nm, of 5 ns (Full Width at Half Maximum – FWHM) at a maximum repetition rate of 10 Hz. The laser beam profile is Gaussian with a spot size diameter of 9 mm.

The fluence (energy per unit of surface) ablation thresholds at the different considered laser wavelengths were determined by identifying the energy at which damage (discoloration and/or material removal) is observed in the sample by inspection under the optical microscope after irradiation in air. The beam size considered for such calculations was determined by measuring the area of the print left on an unplasticized polyvinyl chloride (UPVC) sheet in a single pulse. The irradiations tests at 1064 and 532 nm were carried out through a rectangular mask of $4 \times 6\,mm^2$ without focusing. However, at 266 nm a cylindrical lens with a focal length of 150 mm was used to achieve a rectangular area of $2 \times 6\,mm^2$ on the sample surface. Various conditions of energy per pulse were used. The pulse energy was measured by a power-meter (Gentec ED-200) and modified with a high energy variable dielectric attenuator (LaserOptik). Once the discoloration/ablation fluence thresholds were determined for each system (both for the silver based metals and for tarnish layers), irradiated zones were prepared with fluence values in between the ablation threshold of the base metal and that of the tarnish layer. The changes generated on the tarnish layers can be due both to ablation processes and/or local annealing and melting of the tarnish layers [24].

Table 1 shows the alteration/ablation fluence thresholds of tarnish layers and of pure and sterling silver coupons, together with the fluences used for the cleaning tests. These values are in the same range than those measured by A. Lorusso et al. and A. Buccolieri et al. in references [26,33], using pulses of 30 ns at 248 nm.

For irradiation of the samples, the laser beam impinged perpendicularly onto the target surface which was placed on a motorized XYZ translation stage, where the Z axis is perpendicular to the sample surface. For irradiation at 1064 and 532 nm, the unfocused beam was directed onto the surface of the sample by the help of mirrors. At these two wavelengths, the pulses have enough energy to reach the required fluence for processing the considered samples. Irradiation was performed through a rectangular mask ($4 \times 6\,mm^2$), placed on the surface of the sample, to select the central part of the laser beam and by moving the sample along the direction of the smallest mask dimension. The scanning speed, and consequently the spatial overlap of successive pulses, was chosen to ensure the delivery of approximately 100 pulses on each point of the sample. After processing a rectangular area corresponding to the half area of the sample, this was moved in the transverse direction by steps of 5 mm, resulting in an overlap of 17 % with the previous processed area. To irradiate the whole sample, this operation was done on the two faces. For irradiation at 266 nm, the laser beam had to be focused to overcome the ablation thresholds for the corresponding tarnish layer. To that purpose, a cylindrical lens of 150 mm focal length was used to focus the beam down to $2 \times 6\,mm^2$. Again in this case, the whole surface of the sample was homogeneously irradiated by moving it along the smaller dimension of the laser spot. The chosen speed sample movement ensured irradiation at this wavelength with 100 pulses on each point of the sample surface.

2.3. Characterization techniques

Pure and sterling silver coupons were characterized before and after laser processing by different techniques such as gravimetry, colorimetry, scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS) and micro-Raman spectroscopy.

The mass variation was evaluated using a Mettler Toledo AT261 Delta Range Analytical Balance. Silver based coupons were weighed after each laser cleaning cycle to determine the mass loss. It was noted that the mass increase due to the tarnishing treatment could not be measured because it was lower than the resolution of the balance. A Konica Minolta Portable spectrophotometer model 2500D, equipped with a mask of 8 mm of diameter, D65 illuminant (which corresponds to the average noon daylight from the northern sky

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