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Laser cleaning of tarnished silver and copper threads in museum textiles

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Abstract

Recent developments in laser techniques in the conservation field have allowed us to test the laser cleaning of tarnished silver and copper threads in textiles. The experimental samples were copper and silver plates that had been artificially sulphurised as well as silk bands dyed according to traditional procedures. The experiments were carried out with different Nd³⁺:YAG lasers emitting infrared, visible and ultraviolet radiation. The work has focused on optimising the cleaning process to control the side effects (whitening or yellowing of silver and reddening of copper) produced. Tests were also conducted on real artefacts, and the results are discussed. © 2003 Éditions scientifiques et médicales Elsevier SAS. All rights reserved.

Keywords: Laser cleaning; Tarnished silver and copper; Side effects; Metal–textile composite; XPS analysis

1. Introduction

Cleaning of tarnished metal threads made of silver, gilt silver or copper in textiles is a difficult task, as treatments commonly applied to textile and metals are incompatible. Mechanical cleaning removes the plating. If the threads are made of silver or gilt silver, chemical or electrolytic techniques can be used, but the immersion process may damage the fibres and dissolve any dye [1].

These problems have led conservators to look for other cleaning techniques, including dry methods. Laser techniques seem to be promising here, but most metals absorb relatively strongly at ultraviolet (UV) wavelengths (relative to infrared (IR)). Therefore, irradiation at UV and IR wavelengths might lead to heating of the metal threads, which can be a problem when a composite made of textile and metal is considered.

Our first approach was to test different lasers to determine which radiation levels and cleaning procedures were the most promising. These experiments were conducted at

FORTH—Heraklion, where a large range of lasers is available. The second step was to optimise these results and was conducted at LPIO—Nantes with a Nd³⁺:YAG laser emitting from infrared (1064 µm) through visible (532 nm) to ultraviolet (355 nm) radiation.

2. Preliminary experiments

Different lasers have been used: the BMI 5000 laser Nd³⁺:YAG, which emits infrared radiation ($\lambda = 1064 \mu\text{m}$), and the Nd³⁺:YAG third harmonic laser (obtained by optical isolation of the third harmonic of the Nd³⁺:YAG laser), which emits ultraviolet radiation ($\lambda = 355 \mu\text{m}$). The latter laser is equipped with an articulated arm that can be positioned above the object when it is in a horizontal position on the worktable (Fig. 1). In the case of the Nd³⁺:YAG laser that emits infrared radiation, the samples had to be placed vertically in the path of the laser beam.

The preliminary tests were conducted on silvered brass plates (silvering 20–25 µm), sulphurised artificially by exposure to H₂S vapours produced from a 20%(v/v) ammonium sulphide solution [2], different silver artefacts sulphurised naturally in the atmosphere and original samples of

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Fig. 1. Laser cleaning of fringes with silk core and tarnished gilt silver threads.

metal thread–textile composites dating from the 17th to the 20th centuries. Analysis showed that these metal threads were made of silver, gilt silver or silvered copper.

Results have shown that sufficient cleaning (removal of silver sulphide) was obtained for slightly tarnished pure silver (silvered brass samples) by exposing them beneath the beam produced with the third harmonic laser. The fluence used was as low as $F = 0.08 \text{ J/cm}^2$ (beam maintained for 30 s with a pulse frequency of 10 p/s). The cleaning process was not as good for silver alloys (containing 3.2% Cu) from highly tarnished artefacts [3]. If the fluence is increased (above 0.08 J/cm^2), it causes a surface whitening phenomenon. On fabric samples from real artefacts, similar experiments have shown that the textile is damaged (alteration of the dyes) by the laser impact at a value of $F = 0.16 \text{ J/cm}^2$. With a lower fluence ($F = 0.08 \text{ J/cm}^2$), not only is the textile matrix preserved, but the cleaning also appears to be sufficient. The cleaning can be optimised by modifying the pulse frequency (increasing it from 2 to 10 p/s) and the cleaning time. Cleaning is accompanied by an audible bang, which decreases with the number of pulses. After a certain number of pulses, the surface does not seem to react anymore (the surface appearance does not change, and no more noise can be heard): cleaning has been achieved. Fig. 2 shows the result obtained on a red satin fragment with sulphurised silver threads. Five minutes were needed here to get a good cleaning.

The experimental conditions for the cleaning depend on the material considered and its condition. Metals that are apparently the same, as in the case of tarnished silver and gilt silver as well as partly corroded silvered copper, require different conditions. In the case of silvered copper, another

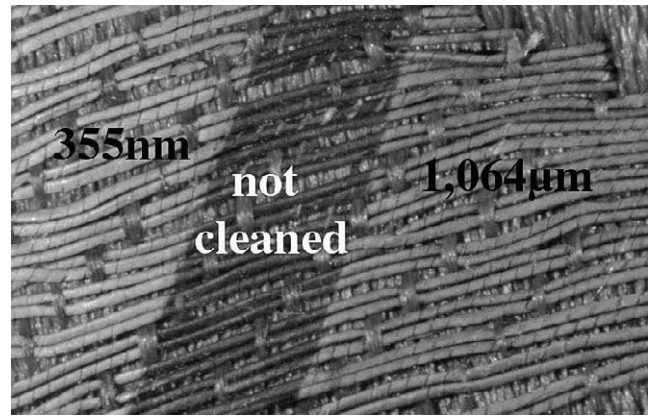


Fig. 2. General view of the silver threads from a red satin fragment treated with different lasers (ultraviolet ($\lambda = 355 \text{ nm}$) and infrared ($\lambda = 1064 \mu\text{m}$)) in comparison to an area that was not cleaned. For the UV experiment, $F = 0.08 \text{ J/cm}^2$, $S_{\text{impact}} = 0.53 \text{ cm}^2$, $f = 10 \text{ p/s}$ for 5 min. For the infrared experiment, $F = 0.35 \text{ J/cm}^2$, $S_{\text{impact}} = 0.55 \text{ cm}^2$, $f = 10 \text{ p/s}$ for 1.5 min.

side effect is provoked: surface reddening. This phenomenon, provoked at fluence as low as 0.08 J/cm^2 (pulse frequency of 10 p/s for 1.5 min), is still not well understood. It might be due to the removal of the superficial silver layer during the laser cleaning or to a redeposition of copper on the metal surface.

The results obtained with the Nd^{3+} :YAG third harmonic laser were found finally to be interesting, but those obtained with the Nd^{3+} :YAG laser were less convincing (dull surface; see Fig. 2). The fluence was much higher here, around 0.35 J/cm^2 for the same pulse frequency (10 p/s), but it was applied for only 1.5 min.

3. Optimisation of the cleaning process

The objective here was to use a Quantel Brilliant Nd^{3+} :YAG laser emitting from infrared ($1064 \mu\text{m}$) through visible (532 nm) to ultraviolet (355 nm) radiation to try to understand the influence of the local environment (with or without oxygen, dry or wet) on silver and copper samples, bare or artificially tarnished ($11 \mu\text{m Ag}_2\text{S}$; similar preparation as above) during the laser cleaning process. The laser beam was fixed, but the samples could be moved transversally on a mobile support (Fig. 3).

As the first tests were conducted with the optimal conditions used previously ($\lambda = 355 \text{ nm}$, $F = 0.08 \text{ J/cm}^2$, pulse frequency of 10 p/s for 40 s), other conditions were also considered in order to speed up the appearance of the side effects. The increase of fluence at 355 nm would have been the best option, but the radiation was quite unstable for that wavelength. Therefore, we preferred to work at 532 nm and $1064 \mu\text{m}$. In addition, argon and helium atmospheres were also used, as shown in Fig. 4, in order to study the effect of de-aerated conditions [4].

In a normal atmosphere (air), results similar to those observed above were obtained during the laser cleaning:

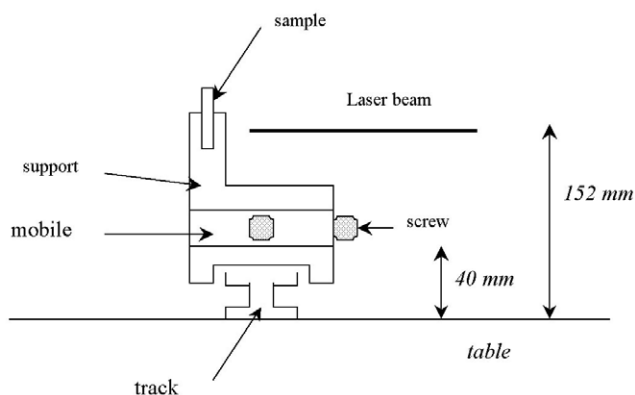


Fig. 3. Support for samples used at LPIO. The orientation of the laser beam is indicated as well as the movement direction of the support.

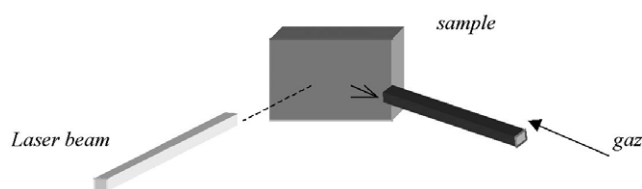


Fig. 4. Schematic representation of the conditions of laser cleaning under argon and helium atmospheres.

using ultraviolet radiation, low energy levels and with a high or low pulse frequency, only partial cleaning was obtained on both bare and sulphurised silver samples. Two side effects were observed: whitening of the surface as the cleaning proceeds and a new yellowing phenomenon, appearing with the laser working with high pulse frequency (10 p/s), that extends from the centre to the edge of the impact as the duration of the cleaning increases (Fig. 5). Audible bangs were also obtained, and it was observed that the sound decreased during the whitening and then increased again during the yellowing. The same phenomena occur in visible and infrared wavelengths, but they are more intense. A closer look at the cleaned surface under SEM revealed an even distribution of prominent tiny particles (5–6 μm) of silver in the white areas (Fig. 6).

Different parameters were assessed to study their effect on cleaning. The influence of the fluence is very important. High values may cause the metal to melt or lead to the formation of craters [5]. Tests were conducted at values of 4.9 J/cm² (pulse frequency = 10 p/s), and these latter phenomena were observed. Spraying the surface with water before cleaning has been proposed by Cooper [6]. Our tests did not show that this parameter had any effect. When the atmosphere was changed to argon, the yellowing side effect was limited. In a helium atmosphere, which has a thermal conductivity 10 times higher than that of argon, no yellowing occurred, but the whitening phenomenon still appeared. Better heat transfer in the material caused a more homogeneous appearance at the site of the impact. Finally, modi-

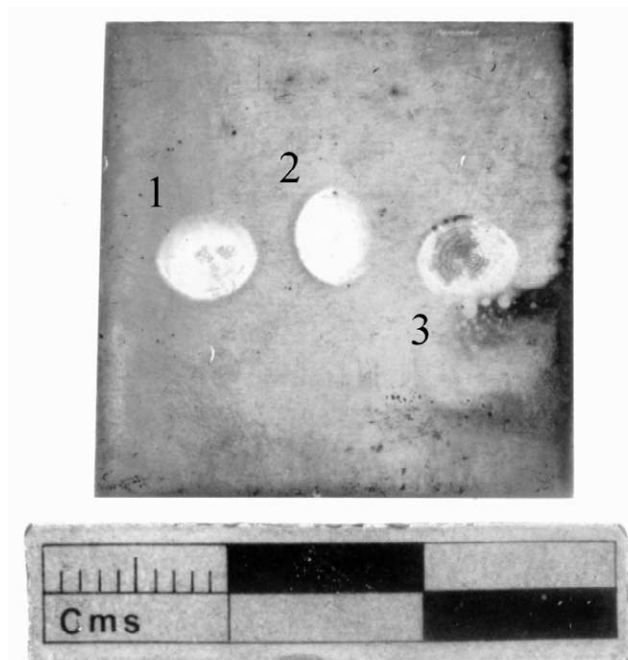


Fig. 5. Examples of laser impacts on an artificially sulphurised silver plate. In air, $\lambda = 355 \text{ nm}$; 1 and 2: 10 pulses; 3: $f = 10 \text{ Hz}$ for 40 s.

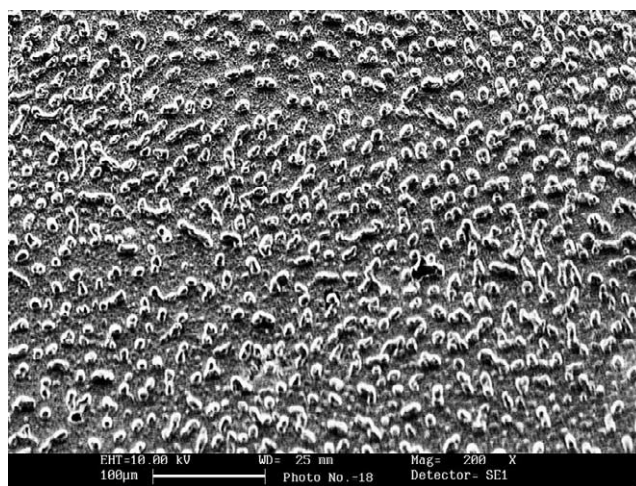


Fig. 6. Detail of an SEM picture showing the presence of prominent silver-based particles corresponding to the whitening phenomenon.

fying the size of the impact with a lens (divergent) allows us to confirm the results obtained by Kearns: with a large impact and a low fluence, wavelike rings corresponding to a partial cleaning were observed in the crater. With smaller impacts, i.e. higher fluence, homogeneous whitening occurred (Fig. 7 and Table 1).

On bare copper, similar phenomena appear, with the formation of surface whitening (a slight audible bang occurs) at a fluence of 1.43 J/cm² and a limited number of impacts (10). Above this value, melting of the metal was observed, and the sound produced increased.

X-ray photoelectron spectroscopy (XPS) has been conducted on untreated silver samples and tarnished silver

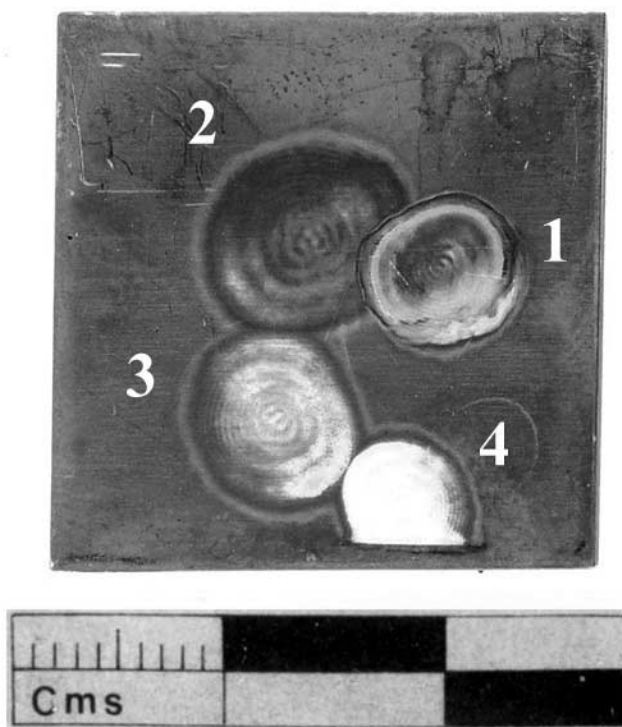


Fig. 7. Influence of the size of the impact (modified with a divergent lens) in a helium atmosphere on the nature of the cleaning process in comparison with the result obtained in air (for data, see Table 1).

samples cleaned in these different atmospheres. Fig. 8 shows that after laser cleaning at 1064 μm , with a fluence of 1.43 J/cm² and a pulse frequency of 10 p/s for 1 min., the 3d5/2 peak of Ag (368.25 eV) is displaced to the right (368 eV) in all the conditions (a little less with helium) and could correspond to the presence of Ag₂O (367.6 eV). However, these differences are quite difficult to evaluate precisely. Other peaks are under study at the moment (C1s, O1s and S2p), and their comparison according to the condition of the experiment could bring more information.

From the previous experiments, it seems then that the surface whitening corresponds to the presence of a superficial layer constituted of globules (5–6 μm), which could be due to silver vaporised during the cleaning process and redeposited on the metal surface. The yellowing, which always appears once the whitening process has occurred, could be due to an excess of heating of the surface causing

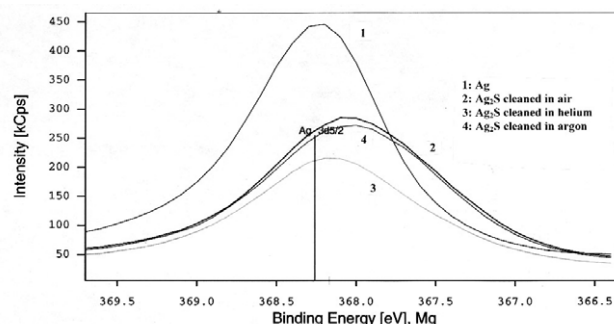


Fig. 8. XPS spectra corresponding to the displacement of peak Ag 3d5/2 according to the nature of the atmosphere during the laser cleaning of silver samples (bare or tarnished) at 1064 μm and $f=10$ p/s for 1 min. Blue: silver; black: silver sulphide cleaned in air; green: silver sulphide cleaned in argon; yellow: silver sulphide cleaned in helium.

the formation of Ag₂O. This oxide can be easily removed by reduction.

4. Application to real artefacts

Based on the optimal conditions determined for the Quantel Brilliant Nd³⁺:YAG laser emitting infrared radiation, under a flux of helium, with a fluence of 1.43 J/cm² and a pulse frequency of 10 p/s for 30 s, cleaning tests were conducted on silk bands dyed using traditional techniques (gaude (yellow), garance (light red) and red wood (strong red)). Under these conditions, the dye colours were not changed, but when similar conditions were applied to a red satin fragment (silk dyed with red wood or garance) containing tarnished silver threads, severe side effects occurred (burning of the textile due to the high temperature obtained during the process; see Fig. 9 (1)). In comparison to the experiments conducted at FORTH, these results appeared much more damaging, but when a smaller number of impacts were applied, the results were acceptable. Cleaning occurs, but the metal looks dull (whitening effect), and a black deposit appears on the silk in the vicinity of the areas cleaned (Fig. 9(2)).

For corroded silvered copper threads, the cleaning is excessive, since the silvering was removed in all the conditions tested (Fig. 10). Similar results were obtained for flag fringes made of gilt silver. The gold layer is removed, and the underlying silver threads appear to be completely cleaned (Fig. 11).

Table 1
Influence of the size of the impact on the nature of the cleaning process (in relation to Fig. 7)

No. sample-impact	Gas	Wavelength (nm)	Pulse frequency (p/s)	Section of the impact (cm ²)	Duration of the treatment	(J/cm ²)
1	Air	1064	2	0.24	2 min 30 s	1.43
2	Helium	1064	10	0.79	30 s	0.43
3	Helium	1064	10	0.56	30 s	0.6
4	Helium	1064	10	0.24	30 s	1.43

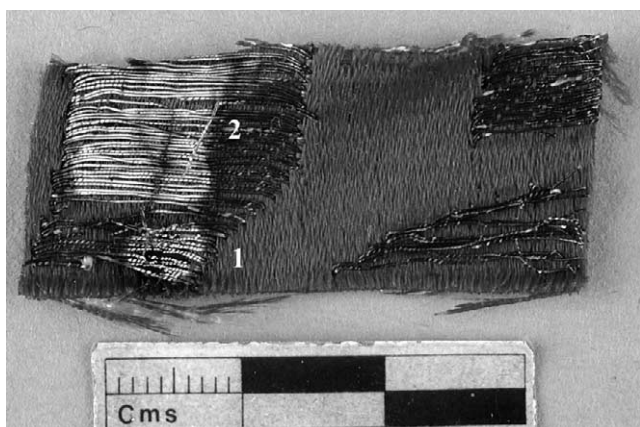


Fig. 9. Effect of laser cleaning with infrared radiation on a red satin fragment under a flux of helium. The fluence is 1.43 J/cm^2 . 1: $f = 10 \text{ Hz}$ for 30 s; 2: 10 impacts. Cleaning of the larger area was achieved by displacing the sample.

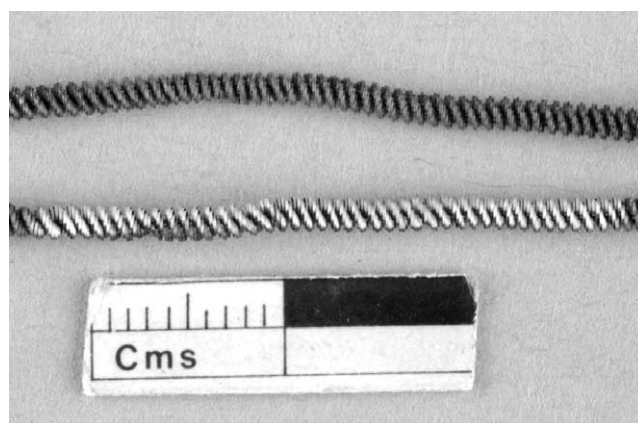


Fig. 11. Effect of laser cleaning with infrared radiation on gilt silver fringes from a flag. Top: uncleaned. The lower fringe was cleaned after several impacts ($J = 0.237 \text{ J/cm}^2$).

Whitening of silver threads causes a loss of brightness, but the original colour of the metal is recovered through the cleaning process. If a lower level of cleaning is applied, less damage occurs, but the surface may take on a gilt appearance that completely modifies the appearance of the material. Before going further, it is then essential to obtain feedback from textile professionals, since they may give precise guidelines for our future work in optimising the cleaning parameters.

Another important question concerns the effect of the laser impact on the long term conservation of the materials. No tests have been conducted to determine how reactive the metal is after cleaning. If it does become more reactive, a cleaning process is perhaps not really advisable, unless the artefact is afterwards placed in a very pure environment. In addition, the effect of laser cleaning on the textile has to be clarified.

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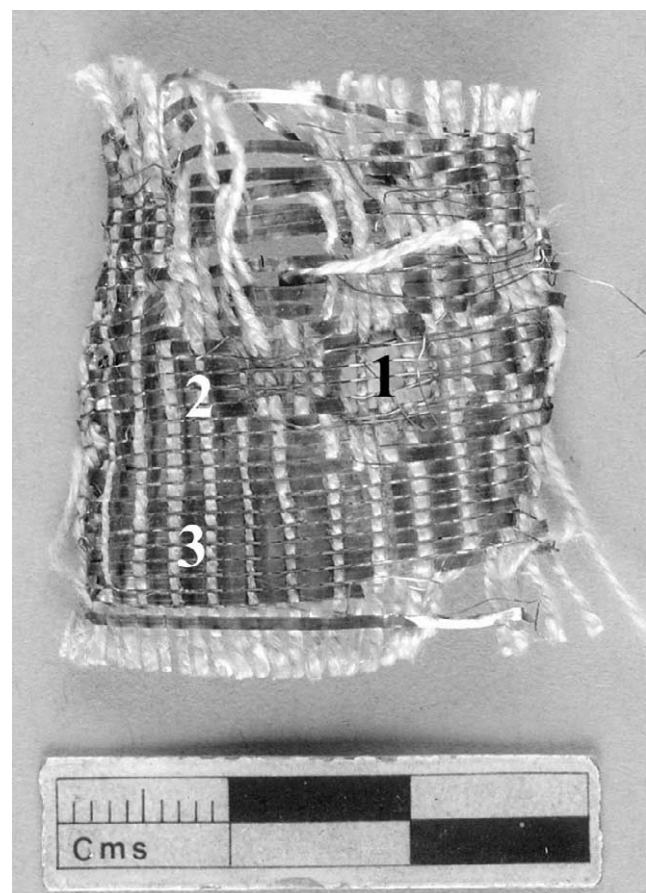


Fig. 10. Effect of laser cleaning with infrared radiation on a lace fragment with silvered copper threads under a flux of helium. 1: $J = 1.43 \text{ J/cm}^2$ and 10 impacts; 2: $J = 0.43 \text{ J/cm}^2$ and 10 impacts; 3: $J = 0.43 \text{ J/cm}^2$ and three impacts.

5. Conclusion and perspectives

Laser cleaning of metal threads appears to be possible, but side effects modify the appearance of the materials. The question is to what extent textile conservators and curators in charge of textile collections will accept this change.