Experimental study on the effect of wavelength and fluence in the laser cleaning of silvering in Late Roman coins

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The political problems in Late Roman Empire caused significant changes in the coin technology. The silver content dropped severely and a new technology was introduced. For the production of these coins, copper based quaternary alloys were used and their surface was covered by a silver amalgam plating layer. Cleaning of these coins, using standard cleaning methods, results in the damage or the complete destruction of the thin silver layer. The main aim of this work was to investigate the use of lasers in the cleaning of the thin silver plating layers found in late Roman coins. The optimisation of laser parameters was achieved through comparative cleaning tests by employing Nd:YAG (532 nm and 266 nm) laser systems. The cleaning results on the plated areas were characterised by optical microscopy and SEM-EDX analysis. Complete removal of the encrustation was observed on the cleaned surfaces, using 532 nm of the Nd: YAG laser.

Keywords: Laser cleaning; Silver amalgam plating; Roman coins; Nd: YAG laser; SEM- EDX analysis

1. INTRODUCTION

The political problems in Late Roman Empire caused significant changes in the coin technology. The silver content dropped severely to less than 5% Ag and a new technology was introduced, which was applied in all the mints operating around the Empire. For the production of these coins copper based quaternary (Cu-Sn-Pb-Ag) alloys were used and their surface was covered by thin silver plating (a few microns thick).

Recent research incorporating analytical, literal and experimental data demonstrated that amalgam silvering was used to plate the coins [1]. Optical microscopy and SEM examination revealed that the coins were subject to severe wear caused by their use and corrosion had affected their preservation. The silver plating layer survived mainly in protected areas and it was covered by layers of copper corrosion products [2].

Hoards of these coins often numbering in thousands have been recovered from across the Empire; however, their conservation has been problematic. The main problem was their cleaning because any attempt to remove the corrosion layers of the coins' surface using standard (mechanical or chemical) cleaning methods resulted in the damage or the complete destruction of the thin silver layer.

Furthermore, the application of electrochemical methods has been used in the cleaning of metallic objects but mainly in the cleaning of silver alloy objects and in particular for the removal of a tarnish layer [3, 4].

The use of laser technology in the cleaning of works of art has a wide range of applications, which includes metallic objects [5-8]. Due to the fact that they are highly controllable and can be selectively applied, lasers can be used to achieve more effective and safer cleaning of archaeological artefacts. Laser cleaning occurs by a combination of mechanisms, the relative importance of each depending on the fluence used and the thermal and optical properties of the substrate and the corrosion products. As a consequence various types of lasers have been used for cleaning metal objects, where Nd:YAG and TEA CO_2 are the most frequent ones. Following systematic laboratory tests and cleaning trials on artworks, the general criteria to select the irradiation parameters are thoroughly demonstrated [5-9].

The main aim of this work was to investigate the use of lasers in the cleaning of the thin silver plating layers found in Late Roman coins. In that particular concept, special care was given to optimization of the minimum removal fluence of the corrosion layer, due to the different composition, surface texture and degree of coherence of the silver plating. Laser cleaning on plated surfaces has only been applied in one case, the treatment of the Gate of Paradise [8, 9]. In this case, the copper alloy substrate was plated by amalgam gilding and for the cleaning a 1064 nm

- Nd:YAG laser was used with varied fluence values from 0.3 J/cm^2 to 0.5 J/cm^2 and 28 ns pulse duration [8].

In this paper, the results of a preliminary study for the cleaning of corrosion layers on plated coins in the laboratory are presented. The optimisation of laser parameters was achieved through comparative cleaning tests by employing Nd:YAG (532 nm and 266 nm) laser systems. Those wavelengths were chosen due to their different optical behaviour on silver and copper [5, 7, 8]. The laser cleaning tests were performed in order to select the irradiation parameters providing corrosion crust removal from the coin's surface without damaging the remaining silver layer. The laser parameters pulse number and fluence values were investigated in constant wavelength, in order to evaluate their influence in the cleaning process.

2. MATERIAL AND METHODS

Two Roman coins from Cope's Archive were used for the purposes of this research. L.H. Cope was a pioneer in the examination of Roman coinage. He used mainly wet chemical analysis for the determination of the chemical composition of the bulk of the coins [10]. The two coins were issued during the period of Licinius, in 315 AD from the mint of Alexandria. Their diameters were from 18.5 to 20 mm. The composition of their substrate alloys, according to Cope's analytical results, is shown in Table 1.

Coin	Ag	Cu	Sn	Pb
Coin 1 (R2)*	2.87	90.76	2.79	3.47
Coin 2 (R3)*	2.95	91.39	2.65	2.66

Table 1 - The alloy contents of the coins according to Cope's analytical results (Data from Cope's Archive)

Optical microscopy examination revealed that the surface of the coins was covered with a corrosion layer consisting of mainly copper corrosion products. There is information on the corrosion of binary and ternary copper alloys [11, 12, 13, 14]. However, the determination of the composition and the structure of the corrosion layers of a copper quaternary alloy have not been fully investigated yet. Despite this, metallographic and microscopic examination revealed that the surface of these coins was covered from a corrosion layer consisted mainly from copper corrosion products [1].

Coin 1 had a uniform layer, which in areas was thicker. Coin 2 however, had an inhomogeneous corrosion layer. On both coins the silver plating was observed under or in between the corrosion layer. Results from the metallographic examination of a coin (R11*), which was issued the same year and the same mint showed that it was made using quaternary copper alloys with a metallographic structure which was typical of a Cu/Sn alloy with, Ag and Pb separately segregated at the grain boundaries. The plating was an applied layer with thickness of 1 micron, which in some areas has suffered from corrosion [1].

The laser cleaning systems consisted of a Q-switched 266 nm and 532 nm Nd:YAG laser with pulse duration of 6 ns at maximum repetition rate of 10 Hz and energy fluence, ranging from 0.1 J/cm^2 to 7 J/cm^2. Then the beam was focused through an appropriate lens of f: 50 mm, onto the sample, which was located on an x-y-z micro-adjustable stage. The controllability of the cleaning level and the damage thresholds of the silver plating were assessed for the two laser systems through various irradiation trials on different test sites.

Optical microscopy was applied in order to examine the coins before the cleaning trials, their surface features and the state of their preservation. Optical microscopy was also applied to evaluate the efficiency of each cleaning treatment.

A scanning electron microscope (FEI Quanta Inspect operated at 25 kV) with an EDAX Genesis ultrathin film window energy dispersive X-ray microanalyser was used after the cleaning experiments to examine the surface microstructure of the coins and to obtain quantitative analysis of the cleaned areas. The analytical data were collected from square area scans. The elements, which were included in the analysis, were Ag, Cu, Sn, Mg, Pb, Cl, Si and Fe.

3. RESULTS

During the cleaning procedure, optical microscopy photographs were taken in order to control the microstructure and texture of the coins surface. The inhomogeneity of the corrosion layer was present on the surface, making the controlled removal of the unwanted corrosion layer from the bulk surface more difficult (Fig. 1)

Figures 1 (a-c) illustrate a defect-rich, inhomogeneous and porous corrosion product layer, where that layer formed over the surface of the silver plating in a more loose manner as reported by bibliography [15]. The deterioration effects from the time upon the silver plating can be seen in the Figure 1a, where fragments of the silver are evident. Different thickness of the encrustation between the peripheral area of the coin, its centre and the letter area is also noticed, as shown from the Figures 1 (a-c). Figure 1 c shows that the corrosion layer has a very thick and porous structure above the silver plating, which due its thickness is not visible at magnification, 4x. The tests were carried out using different laser sources, and useful indications of the lasers suitability were deduced.

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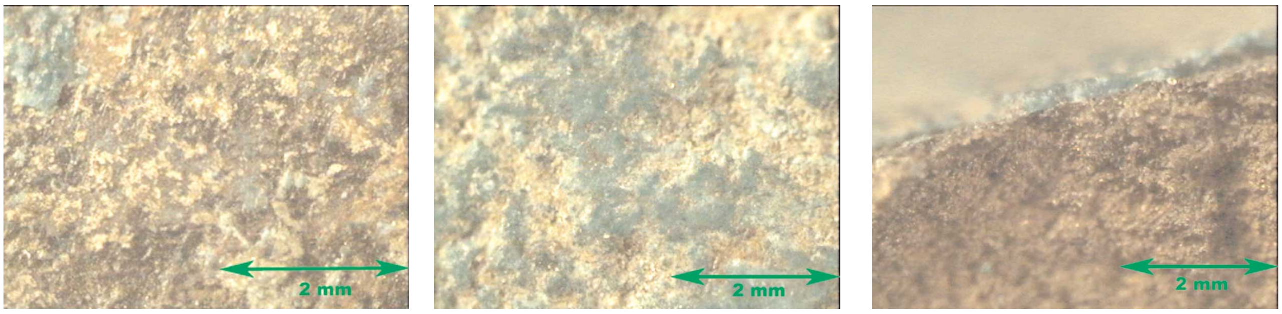
* The codes R2, R3 and R11 belong to Cope's coin reference system, which was followed by the following researchers.



a b c

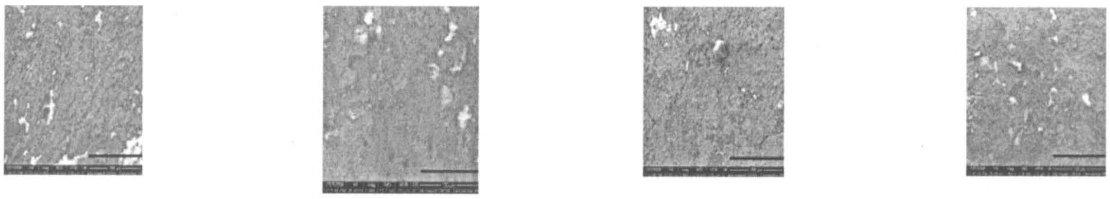
Figure 1 - Microscopy photos and a stratigraphic analysis of the corroded coins, with a magnification bar (⁻) of 2 mm shown at the right-bottom side of the photos

A representative overview of irradiation trials, of cleaning versus different fluences at 532 nm, with one laser pulse at the coin 1 is shown in Table 2. Optical microscopy was applied in order to assess how successful was each trial and which was the condition of the silver plating layer after cleaning. Other characteristic features of the laser cleaned areas that were examined were whether there was evidence of blackening or melting.

Trials	Fluence J/cm^2	Corrosion removal	Condition of the plating layer	Blackening	Melting
1	0,39	good	traces	a little	no
2	0.86	partial	damaged	a little	no
3	0.90	partial	good	traces	no
4	0, 93	good	very good	traces	no
5	0.94	good	very good	a little	no
6	0.98	good	very good	no	no
7	1.00	good	very good	no	no
8	1.02	partial	damaged	a lot	no
9	1.10	good	good	traces	no
10	1.25	good	good	a little	no
11	1.27	partial	damaged	a lot	no
12	1.34	good	damaged	a lot	no
13	7.10	partial	damaged	a little	no

Table 2 - Trials of cleaning versus different fluences at 532 nm with one laser pulse at the coin 1

For further quantitative research of the laser cleaning with the 532 nm-Nd:YAG SEM/EDX analysis was invoked (Fig.2). From the Figure 2(a-h) the morphology shown after laser cleaning with the above fluencies displayed different cleaning behavior, which was confirmed by the percentage analysis of the element concentration.



a) 0.90 J/cm^2 b) 0.93 J/cm^2 c) 0.94 J/cm^2 d) 0,98 J/cm^2

e) 1.00 J/cm^2 g) 1,10 J/cm^2 f) 1,25 J/cm^2 h) 1, 34 J/cm^2

Figure 2 - SEM Photos of the irradiated areas of coin 1 vs fluence values of 532 nm, with a magnification bar (⁻) of 100 μm shown at the right-bottom side of the photos

From the Table 2 we focus our attention to three fluence values (0.93 J/cm^2, 0.98 J/cm^2 and 1.00 J/cm^2), at which we obtain a better cleaning behavior. Quantitative analysis by SEM-EDAX of the surface of the coin 1, after laser cleaning in three areas, where the plating layer was in very good condition, showed that the cleaning was successful (Fig. 3, Tables 2, 3).

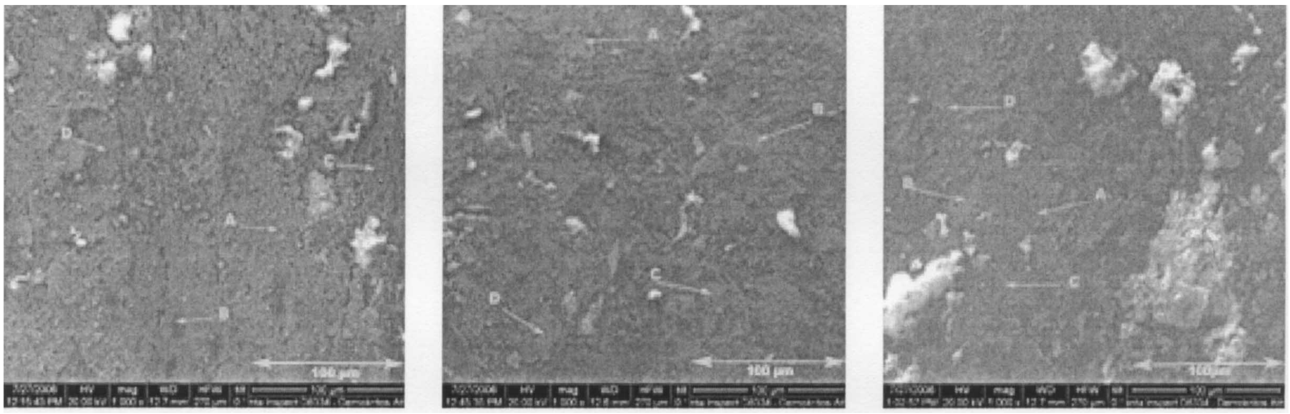


Figure 3 - a) SEM photo of the morphology of the coin 1 surface (0.93 J/cm^2) b) SEM photo of the morphology of the coin 1 surface (0.98 J/cm^2) c) SEM photo of the morphology of the coin 1 surface (1.00 J/cm^2)

The morphology of the coin 1 surface, after the irradiation with the selected fluencies, is shown in Figure 3, with a magnification bar of 100μm shown at the right-bottom side of the photos. Table 3 shows we have the quantitative analytical results after laser cleaning.

Fluence, J/cm^2	Area	Ag	Cu	Sn	Mg	Pb	Cl	Si	Fe
0.93	A	72.66	18.91	2.52	0,95	3.85	0.16	0.51	0.44
	B	65.31	29.20	1.58	0,55	1.95	0.31	0.59	0.52
	C	52.30	37.98	4.74	1,01	2.06	0.52	0.75	0.66
	D	82.20	11.35	1.92	1,44	2.07	0.20	0.41	0.42
0.98	A	83.72	09.16	2.55	1,37	1.63	0.31	0.51	0.75
	B	83.62	10.89	2.84	1,58	0.00	0.33	0.23	0.68
	C	86.21	06.31	1.43	1,29	2.18	0.79	0.35	0.41
	D	75.62	14.69	1.17	1,16	3.52	1.34	0.96	0.47
1.00	A	82.79	11.52	1.99	1,30	1.16	0.14	0.49	0.61
	B	85.48	10.89	0.89	1,58	0.00	0.25	0.49	0.42
	C	84.20	08.38	2.11	1,7	2.18	0.19	0.69	0.55
	D	79.26	11.44	1.17	2,22	3.19	0.33	0.90	0.49

Table 3 - Quantitative analysis of the percentage elemental concentration of coin 1, irradiated by 532 nm with one laser pulse, for the above irradiation tests (Fig 3)

According to Table 3, the high concentration of silver is indicative of the presence of the silver layer on the surface, while the corrosion products containing chlorides are minimal. At the same areas the alloying elements of the copper alloys are in low concentration. We confirm that with that range of fluence values the corrosion products are removed successfully, without any damage of the silvering. Silver appears in range of 68-83%, while copper is around 10%-24%. It is shown that at the fluence of 0.93 J/cm^2 we have a satisfactory cleaning, but few percent of the silver layer is revealed while at 0.98 J/cm^2 and at 1.00 J/cm^2 the ratio of the Ag/Cu increases, with the present of chlorides to be less at the 0.98 J/cm^2 fluence value.

At the Table 4 representative irradiation trials from the laser irradiation process of the coin 2, with the 266 nm of Nd:YAG laser, with thirteen laser pulses, are shown. Discoloration or melting of the surface occurred when the energy density or pulse repetition frequency was high (above 1 J/cm^2). Due to the low melting temperature of the surface composition it was suggested that the laser should be operated with a controlled repetition rate, in order to allow us to estimate the damage threshold. From the results, the 0.35 J/cm^2 found to be more satisfactory, in relation with the other fluence effects on that coin. But when trials of repeated laser scanning were carried out, melting of the surface was noticed.

Trials	Fluence (J/cm^2)	Corrosion removal	Silver plating is observed	Blackening	Melting
1	0.35	partial	No	no	a little
2	0.54	traces	No	a little	a little
3	0.82	traces	No	a little	a lot
4	0.95	traces	No	a little	a lot

Table 4 - Trials of cleaning versus different fluences at 266 nm with thirteen laser pulse at the coin 2.

4. DISCUSSION AND CONCLUSIONS

The aim of this paper was to find the optimum wavelength and fluence processing for safe cleaning of the surface of plated Roman coins. It was determined by measuring the damage threshold laser fluence on the silver layer and the required fluence for complete removal of the corrosion products. Damage thresholds were deduced from the analytical methods used, where melting, removal, or other damage could be observed, estimated and quantified. Increase of the cleaning efficiency with an increase of laser fluence was expected, but the results showed an optimum fluence window between 0.93 J/cm^2 and 1.00 J/cm^2. According to the Tables 2 and 3 and the Figure 2, at those fluences the high concentration of silver is indicative of the presence of the silver layer on the surface. In these areas corrosion products diminished and more homogeneous cleaning was evident.

Experimental results at 532 nm showed the variability in the removal of the corrosion due to the different corrosion composition and thickness in the irradiated area of coin 1. Other researchers indicated that an average corrosion thickness on a great number of bronzes from the Bronze Age to historical periods is in the range 10-250 μm when the alloy core is still present. In most of the cases the corrosion consists of a well adhering single layer, of which the appearance is variable depending on the sample and the location of the corrosion on the sample [16]. Although the thermal diffusion lengths of pure Cu and Ag for a pulse duration of 6 ns are approximately 1.7 μm and 2 μm respectively, much less than the average thickness of the corrosion layer, the co-existence of corrosion products of Ag and Cu in some areas, where the encrustation layer is thinner, increases the thermal diffusion length and the material removal is less confined on the corrosion surface [6, 8].

Experiments with low values of fluence irradiation at 532 nm did not revealed any reaction from the surface, while after a large number of laser pulses a blackening of the corrosion area was displayed. Below the approximate cleaning threshold, the laser seemed to cause the surface to go black with a faint greyish tinge. Once there was a change of color, the laser irradiation was absorbed more readily and further damage could easily occur. A possible explanation for that behaviour could be justified by an entirely different laser beam material interaction which is taking place, at low fluencies, below the cleaning threshold, involving further oxidation of the Cu_2O to CuO [7].

Experimental results at 266 nm on coin 2 showed us the unsuitability of that wavelength to clean the corrosion layer. It is known that most metals absorb relatively strongly at ultraviolet (UV) wavelengths, as compared to the infrared (IR) wavelengths. Therefore, irradiation at UV wavelengths might lead to heating of metal artefacts. Thus, this heating can be a problem when an artefact made of copper alloy with a fragile silver plating layer is considered. The reflectance of Cu and Ag at that wavelength is much lower (0.33 and 0.24 respectively) than those at the wavelength of 532 nm (0.61 and 0.95 respectively) [17]. As a result, although the irradiation process did not reach the melting point of the situated metals, even in very low fluencies it induced partially melting of the corrosion, which caused difficulties in the removal of that layer. The use of pulsed 266 nm laser, for cleaning corroded silver-plating copper alloys metals is thus limited by the risk of surface melting and blackening due to thermal and photochemical effects.

From these preliminary experiments, we conclude that the case of corroded silvered copper alloy coins, require different cleaning conditions than other corroded copper coins. From the two laser wavelengths 266 and 532 nm, which were employed, the second harmonic of Nd:YAG was more controllable and promising. The copper corrosion products appeared to have different optical behavior.

Additional work has to be made to those and to other laser wavelengths, in order to minimize the chances for thermal diffusion, during the laser cleaning process, so as the laser absorption depth to be limited to the thin layer of corrosion near the surface. Therefore there is a great need to continue the investigation of cleaning techniques that will not only improve the cleaning efficiency of those silver plated objects but also minimise damage to the critical surfaces of silver plating layer during the cleaning process.

ACKNOWLEDGEMENTS

This research effort is financially supported by the General Secretariat of Research and Technology of Greece, Joint Research and Technology Programmes, Greek-Italian Cooperation Program 2006-2008 (and particularly the Project “Characterizations and cleaning of metal artefacts by lasers”). We would like to acknowledge also the Department of Coins and Medals, British Museum for allowing access to Cope’s Archive. Finally thanks are due to Dr. A. Travlos for his kind cooperation with the SEM measurements.

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