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LASER CLEANING OF CORROSION, EFFICIENT AND ENVIRONMENTALLY FRIENDLY METHOD

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Abstract
In recent years, lasers have been used more and more in different areas of human life, science, industry, medicine, military, agriculture, and show business, protection of environmental and cultural-heritage objects, in the arts and so on. Laser technology has some advantages in many areas over classical methods. This paper presents the results of laser application for cleaning corrosion of metal objects, cooper and brass. The first sample was oxidised cooper plate and the second ashtray made of brass. Nd: YAG laser was used as a source of radiation to clean surface corrosion deposits. Removal of layers from the surface occurs through the process of laser ablation. Three wavelengths were used with different fluences. The cleaning results, i.e. the morphological and chemical changes were investigated by optical microscopy, XRF analysis and colorimetry. The obtained results show that lasers are efficient corrosion cleaning and environmentally friendly method.

Keywords: laser cleaning, metal, corrosion, Nd:YAG laser, cultural heritage

INTRODUCTION

Corrosion is a problem for all metallic objects. Corrosion is the destruction of metals and alloys due to chemical or electrochemical reaction with the surrounding environment. Electrochemical corrosion is a consequence of electrochemical reactions and is subject to the laws of electrochemical kinetics. The important condition for its appearance is the contact of the metal with the second phase, which has the properties of electrolytes, whereby the metal creates a thin layer with the properties of the electrochemical double layer. This includes all cases of corrosion in a humid atmosphere, as well as corrosion of metals in electrolyte solutions [1].

Pollution of the environment is a major problem facing the modern world that leads to the destruction of eco system, the achievements of civilization and cultural heritage. Interest in the use of laser technologies in this area is caused by the catastrophic degradation of the monuments in recent decades, which is the consequence of the increasing effect of anthropogenic factors. The distressing state of many architectural monuments, sculptures, historical buildings, and museum artefacts and the acceleration of their breakdown processes request the use of new and effective technologies for restoring and preserving such objects. The study and conservation of museum collections request the application of scientific methodology in the examination, analysis and dating of objects. In all these methods, lasers play an important role [1].

The conventional techniques of metal surface cleaning are based on mechanical or chemical methods which can lead to the substrate being damaged or polluted. There is numerous literatures [1–11] that describes the classic and laser methods and problems accompanying their implementation in cleaning and protection of metals. It can be conclude that lasers can to change some classical, pollutant method with ecological friendly ones in different applications. Lasers cannot prevent pollution or reduce the concentration of harmful substances, but can detect pollutants and determine in which amount are present.

Laser cleaning is of interest due to its great potential for removing contamination or films from different substrates [3]. Lasers have many advantages over conventional techniques. They can be used for contactless and fast surface cleaning and processing (drilling, marking, grooving, cutting and welding) with precisely controlling energy deposition in the material.

Precisely controlled laser cleaning features a unique feature: removes impurities and corrosive products from the surface without damaging the base surface. Laser systems are very efficient, economical, and environmentally friendly compared to existing conventional methods. They do not require chemicals and abrasive materials, or storage for waste disposal. Laser, mobile systems, equipped with different types of lasers can be impulsive or continuous, with high mean power. These can be equipped with an optical cable up to 50 m long, making them suitable for applications such as historical monuments, high voltage pylon cleaning, metal contaminated parts of nuclear plants or facades of large cultural heritage sites. Laser cleaning is applicable in the automotive industry. Lasers can be used for welding, removal of oils and lubricants, cleaning of electronic components and cleaning of tools. Lasers can also be used in the food industry. In the airline industry, laser cleaning is most used in the removal of colours and other coatings from the surface of the aircraft. Lasers can also be used effectively in the selective sintering of different materials.

Many studies [4,5,11] confirm that Nd:YAG lasers (l = 1.06 mm), with ns pulses, are highly effective in removing inorganic encrustations from artifacts; however, the absorption of laser radiation by bulk material can raise the surface temperature and can cause some changes. Because of that, every investigation of Nd:YAG laser ablation is of great interest for laser application in the cleaning process.

MATERIALS AND METHODS

In this paper are presented the results of cooper and brass laser cleaning. The first sample was oxidised cooper plate and the second ashtray made of brass [11].

All experiments were performed in laboratory and normal atmospheric conditions. Nd:YAG laser, Thunder Art Laser, produced by Quanta System (with wavelengths $\lambda = 1064$ or $\lambda = 532$ nm, optical pulse duration < 8 ns, and output pulse energy up to 1000 mJ) was used in the presented experiments. The repetition rate is up to 20 Hz, with a beam diameter of 10 mm and 70 % fit to Gaussian energy distribution. The lens with focal length of 150 mm is used to focus laser beam.

Copper is a metal that has been used for millennia for a wide variety of purposes, and today it is irreplaceable in electronics, computer industry, energy, construction and medicine. Numerous objects of cultural heritage are made of copper or its alloys, bronze and brass. Laser cleaning of copper surfaces is very important with several aspects [1,7].

The experimental parameters are provided in Table 1. The laser cleaned objects are presented in Figure 1. The dimensions of corroded cooper and brass plates are 50x30x1 mm and 60x30x2 mm, consequently. The relief ashtray belongs to a private collection, dated to the beginning of the twentieth century.

The results of laser beam-material of the samples were recorded with the optical digital USB microscope with different magnification. Chemical composition was determined by XRF analysis and the colour changes by colorimeter [11].

a) *b)*

***Figure 1** a) Oxided cooper and brass plates with laser cleaned zones, b) ashtray*

***Table 1** The experimental conditions during laser cleaning of some zones on cooper and brass plates and ashtray*

Oxide cooper plate					Ashtray				
Zone number	f, Hz	t, s	E (mJ)	λ, nm	Zone number	λ, nm	E, mJ	f, Hz	t, s
		cooper			1	1064	250	20	5
1	20	5.5	500	1064	2	1064	350	20	5
3	20	4	500	1064	3	1064	450	20	5
5	20	5	200	532	4	1064	600	20	5
		brass			5	1064	750		5
2	10	3	500	1064	6	532	375	20	5
5	20	5	500	1064	7	532	375	20	240
7	20	4	200	532	9	1064	600	20	240
					10	355	250	20	240
					11	Mechanically cleaned			

RESULTS AND DISCUSSION

Surface cleaning, based on laser ablation, is a delicate and irreversible process, followed by many potential complications. It is very important to choose the most suitable laser cleaning methodology and laser parameters in accordance with the material properties. Laser ablation occurs when the laser fluence (pulse energy per unit area) overcomes a critical threshold, which is an intrinsic property of the material structures under irradiation.

The application of laser in cleaning the corrosion layers on metallic threads is a complex phenomenon, depending on characteristics of laser lights and materials. It is based on several processes: absorption of laser energy within a very short period of time (several ns), melting of material in the heating layer depending on the applied energy, and ablation or evaporation of material. Depending on the fluence and quantity of absorbed energy, mechanical, expansion waves can be formed, consisting of evaporated material and ambient gas, which also rips off parts of the surface layers and discards them from the irradiated zone. The strength of the expansion wave increases if the sample is damp, and thereby creates conditions for more efficient cleaning of corrosion products. A laser re-melting process is the fundamental process, which occurs in parallel with the cooling of the melted layer.

Microscopic tests, conducted by optical microscopy, allow the study of the threshold of ablation fluence and efficiency of cleaning process. Figure 2 shows some zones on cooper and brass plates cleaning with parameters presented in Table 1. The analysis of images show that the corrosion is removed, but some colour changes occur in and around irradiated zones (in HAZ). It can conclude that laser radiation (1064 nm, 8 ns) at fluence levels above 0.6 J/cm^2 causes some melting to copper and brass. Brass appeared to be the most sensitive of the metals tested.

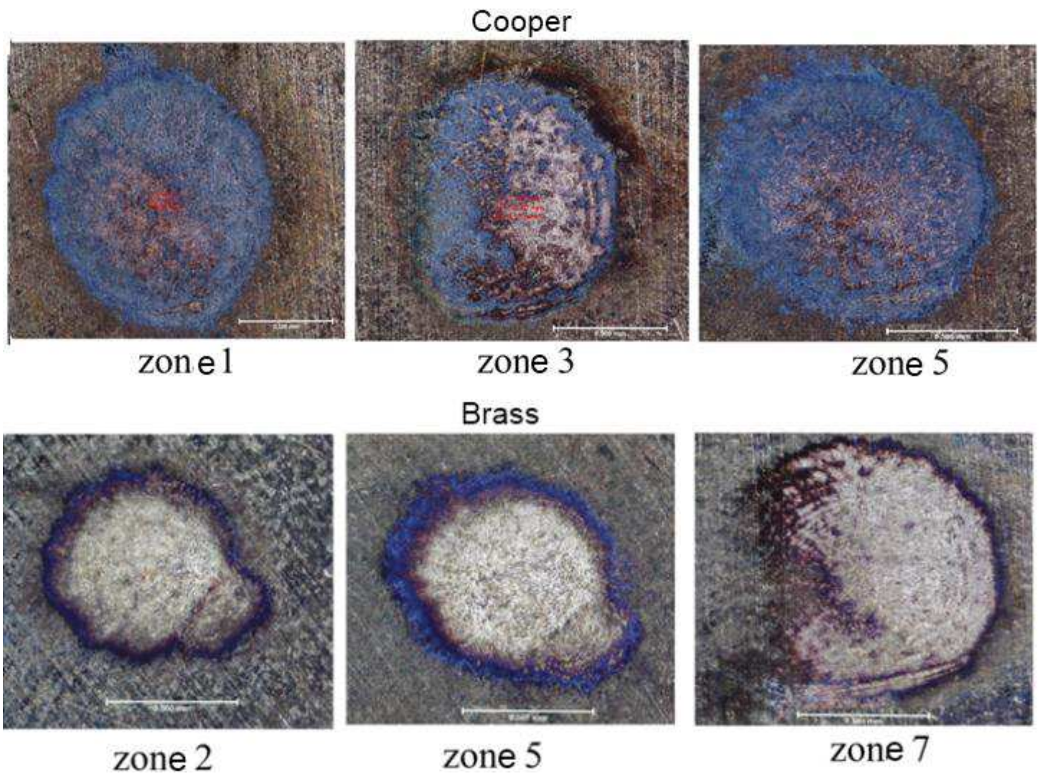


Figure 2 *OM of laser cleaning zones on brass and copper plate*

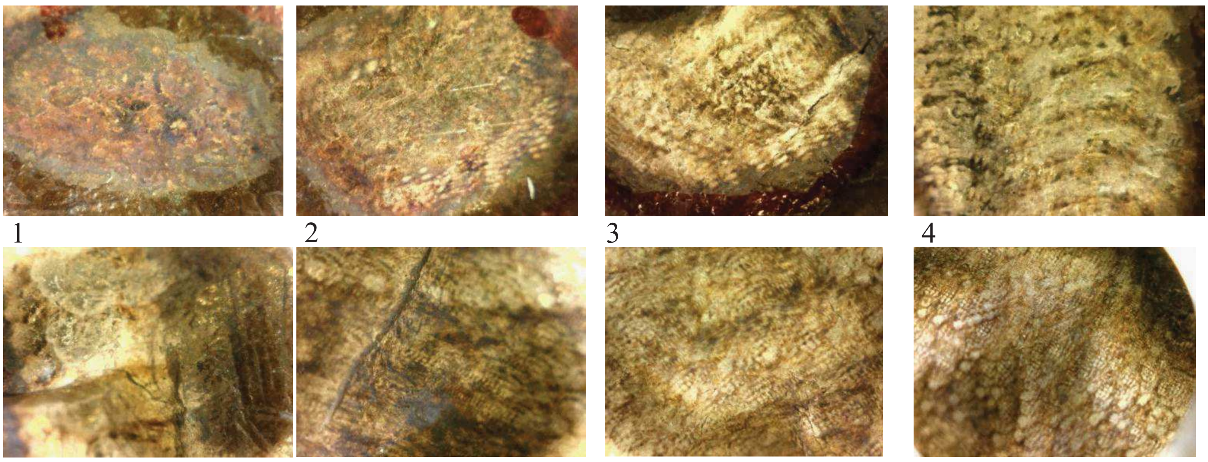
Figure 3 presents the appearance of the ashtray after partial laser cleaning (rear side) with laser treated zones. Experimental conditions during laser cleaning are given in Table 1. In these studies, the laser parameters have been selected very carefully and they are below the material damage threshold.

Chemical composition determined by XRF analysis on laser treated and untreated zones, (table 2) points to the fact that there is no coating, there is a thin layer on the surface of the sample that is corroded and which protects the surface against further corrosion. Since the chemical analysis is carried out by XRF method, which cannot detect light elements, it is very likely that on the surface of the ashtray, besides the oxide layer, there is a thin layer of organic materials, which during the laser irradiation leaves dark clues.

Table 2 *XRF analysis of ashtray [11]*

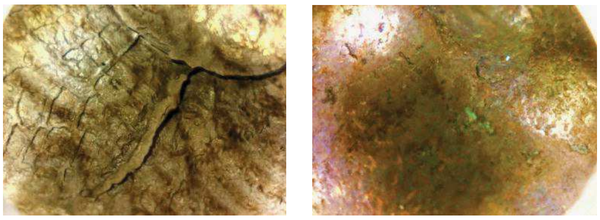
Zone	Concentration % $\cdot 10^{-3}$													
Elements	Sb	Sn	Ag	Mo	Nb	Pb	Zn	Cu	Ni	Fe	Mn	Cr	V	Ti
Cleaned	17	845	159	5	6	2564	35488	59043	755	580	150	140	159	46
Uncleaned	17	870	159	5	7	2562	33383	59089	754	599	140	164	170	44

Figure 3 *Laser cleaning of ashtray rear side*



1 2 3 4

5 6 7 8



9 10

Figure 4 *OM analysis of laser cleaned zones*

The images in Figure 4 are made with a USB optical microscope, with a magnification of 40x. An analysis of the images confirmed the inhomogeneity of surfaces that were cleaned by the laser. Around the zone 1-3 appears dark ring, while in the zone cleaned by the scanning laser beam with constant velocity, periodic segments of curved shape are formed.

The results of colorimetric tests for uncleaned surface and for zone 9 are presented in Figure 5. The analysis of the surface colour was based on the L∗a∗b parameters.

a) *b)*

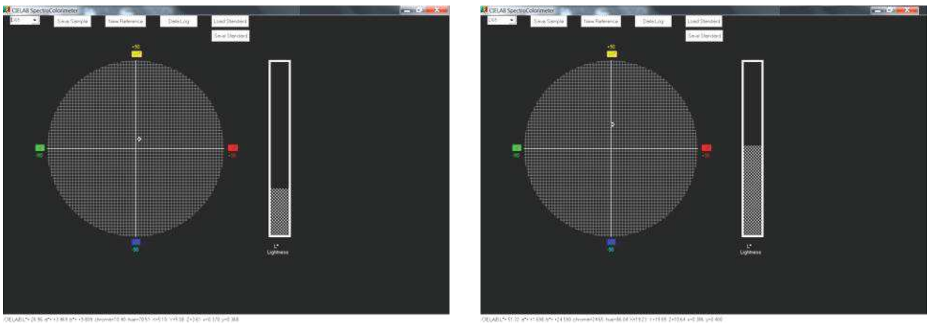


Figure 5 *Colorimetry of: a) uncleaned zone, b) zone 9*

CONCLUSION

From the results of the conducted tests, it can be concluded that the use of a Q-switched Nd:YAG laser at 1064 nm and 532 nm is suitable method of cleaning thin corroded layer on copper and brass objects. According the obtained results the ablation threshold fluence for oxidized layers from cupper surface is estimated below 0.5 mJ/cm^2. Localised surface melting was found to occur at this fluence. The ablated layers evaporate and it is only one by-product of cleaning. No other pollutant in laser ablation. Because of that, laser technology is environmentally friendly and is becoming more and more applicable.

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REFERENCES

[1] S. Polic-Radovanovic, S. Ristic, B. Jegdic, *et al*., Metodološki i tehnički aspekti primene novih tehnika u zaštiti kulturne baštine, Institut Goša and CIK, Beograd, (2010), ISBN/ISSN: 978-86-86917-12-06 (in Serbian).

[2] C. Fotakis, D. Anglos, V. Zafiropulos, *et al*., Lasers in the Preservation of Cultural Heritage: Principles and Applications, CRC Press, 2005, p. 335.

[3] Y.S. Koh, Laser Cleaning as a Conservation Technique for Corroded Metal Artifacts, 2005, Doctoral Thesis, Luleå, Sweden, p.114.

[4] H. Garbacz, E. Fortuna, J. Marczak, *et al*., Applied Phisics A; 100 (2010) 693–701.

[5] A. Koss, J. Marczak, Application of lasers in conservation of monuments and works of art, 2005, Scientific reports IAICR 1, 50 pages, ISBN: 83-922954-0-4.

[6] M. Tang, *et al*., Journal of Laser Micro/Nanoengineering; 6 (1) 2011 6–11.

[7] B. Radojković, S. Ristić, S. Polić, *et al*., J. Cult. Herit; 23 (2017) 128–137.

[8] S. Bashir, H. Vaheed, K. Mahmood, Applied Physics A; 110 (2013) 389–395.

[9] H. Kadhim, I. Ghazi, A. Hussein, Engineering & Technology Journal; 34 (7) (2016) 1439.

[10] C. Korenberg, A. Baldwin, Laser Chem; (2006), Article ID 75831, p. 7, doi: 10.1155/2006/75831.

[11] S. Ristić, B. Radojković, S, Polić, Savremene metode laserskog čišćenja predmeta kulturnog nasleđa, NU IHTM, CIK, Beogradu, 2018, pp. 1–420, ISBN: 978-86-81405-25-3 (in Serbian).

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