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Research Paper

Femtosecond Laser Cleaning of Archaeological Cultural Assets

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Abstract: This study presents research on femtosecond laser ablation of corrosion crusts from ancient coin. On the surface of ancient coin sample was irradiated with 800 nm laser wavelength, 90 femtosecond laser pulses in duration, and 1 kHz repetition rate. Femtosecond laser ablation was carried out by changing laser intensity using from 1.96 x10^{13} W/cm^2 to 9.82 x 10^{14} W/cm^2 in atmospheric conditions. Scanning electron microscope and optic microscope images were recorded and scanning electron microscope- energy dispersive X-ray spectroscopy graphs and reports were recorded. The used coin belonged to the near Roman Imperial Age where the copper-zinc alloy was used for coins. The amount of copper and zinc ratios before and after application of laser ablation procedure is reported by courtesy of scanning electron microscope-energy dispersive X-ray spectroscopy graphs and reports on surface of coin. Scanning electron microscope and light microscope images show that laser intensities above 9,82 x10^{14} W/cm^2 perform an effective cleaning process.
Keywords: *Femtosecond, Laser Cleaning, Coin, Copper, Zinc*

Introduction

In metallic artworks, materials can be affected by corrosion caused by atmospheric conditions, moisture, and water (Buccolieri et al., 2014; Petiti *et al.*, 2020; Serafetinides *et al*., 2009). Historical materials can be cleaned widely using chemical agents, electrochemical and mechanical methods (Al-Sadoun & Abdel-Kareem, 2019; Di Turo, 2019; Viljus & Viljus, 2013). Chemical agents can be used for the removal of corrosion or other layers of contaminants from the surface of cultural heritage objects and monuments. The Laser ablation process is used to remove of the corroded layer and other contaminants on the surface of artworks (Abdel-Kareem *et al*., 2016a; Abdel-Kareem et al., 2016b; Palomar *et al*., 2016). Different laser pulse durations have been used to clean such historical materials and performed and reported successful results (Bilmes *et al.*, 2018; Dajnowski, 2013; Siano *et al.*, 2012; Strlič *et al*., 2003).

Lasers provides some beneficial advantages to remove of corroded layer from the surfaces due to non-hazardous and non-toxic effects. Laser pulse power and also laser pulse duration have very important effect on removal of the undesired materials from the surface of artworks (Drakaki *et al.,* 2004). Laser removal process of the corroded layer has been one of the cleanest techniques in restoration works (Antonopoulou-Athera et al., 2019; Di Francia et al., 2018; Korenberg & Baldwin, 2006; Nevin *et al.,* 2007; Zanini *et al.*, 2018). The purpose of the corrosion removal process is to create a homogeneous surface in accordance with the original surface without damaging the material *(Pouli et al.,* 2012). Laser technology allows desired cleaning performance to remove unwanted/aged varnish layers from paintings (Chillè et al., 2020; Pouli *et al*., 2012).

Femtosecond (fs) lasers are known as a powerful technology for material processing studies. Pulse duration and pulse power are effective parameters on the surface cleaning process of materials. In the case of long laser pulse duration such as ≥10 picoseconds, some energy deposition can be taken place on the surfaces of arts due to higher temperatures which causes non equilibrium surface modifications

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(Siano & Salimbeni, 2010). Fs laser technology doesn't deliver heat transfer to materials due to ultra-short pulse durations (10^{-15}s) when are very shorter than heat transfer duration (10^{-8}s) of the materials (Burmester et al., 2005; Ersoy et al., 2014; Korte et al., 2003). The advantages of fs laser pulse duration have already been reported elsewhere by several groups in the literature (Burmester *et al*., 2005; Georgiou *et al*., 2008). In the process of laser-material interaction, it is important to protect the original parts of historical materials during ablation process. Before laser cleaning of a sample with a historical artefact, laser parameters should be evaluated by performing a preliminary study on a material without a historical value. Thus, the negative effects that may occur during the cleaning of the sample, which has the characteristics of historical artefacts, will be eliminated, and protected. (Buccolieri et al., 2014; Koh & Sárady, 2003; Maharjan *et a*l., 2017). Fs laser-material interaction process gives precise, pure ablation for solid targets when compared to nanosecond and picosecond laser ablation processes (Chichkov et al., 1996). It is known that the laser pulse duration and laser wavelength effect the laser-material processing without any damage on the surface of cultural heritage objects (Koh & Sárady, 2003; Pini *et al*., 2000; Siano & Salimbeni, 2010).

Femtosecond (fs) laser is generally used in laser ablation technique because it is more appropriate for quantitative principal analysis relative to nanosecond (ns) laser due to better reproducibility of plasma features (lower relative standard deviation, RSD) (Kalam *et al*., 2020) Fs laser has been utilized in several applications such as classification of plastic polymers (Lasheras et al., 2010), archaeological studies (Muhammed Shameem *et al*., 2020; Remus et al., 2010), and geological studies (Gondal et al., 2009; Harmon et al., 2009; Harmon et al., 2013; Kalam et al., 2020; Wickramasinghe, 2021). Restoration of archaeological metal objects includes a complex and multistep process that contains the object's analysis, strengthening its surface and internal structure, corrosion stabilization, preservation, reconstruction of components, and replenishment of losses. Cleaning of abrasive layers has a critical role due to the possibility of removing contaminations, suggesting the shape of the object being restored and its technological and decorative features. Recent studies have recommended several methods for cleaning metal objects (Craddock, 2009; Scott, 1994). Laser cleaning is a promising approach, which can solve some complicated restoration tasks as the cleaning of objects with inlays. Fs lasers present pioneering cleaning facilities to reveal the information about the investigation of some historical materials such as coins (Abdel-Kareem et al., 2016a), parchment papers (Ersoy *et al.,* 2014; Walczak *et al*., 2008), wood or soil based cultural heritage objects (Kaminska *et al.,* 2005). It has been presented that copper-zinc alloy coin determines optimal conditions for removal of acorroded layer.

In this study, a historical coin, which was made of copper-zinc alloys was used for ablation process to investigate the effectiveness of 800nm wavelength for cleaning surface corroded layers. Hence, a series of experiments were performed using laser power values ranging from 10-500 mW per pulse and several repetitive applications were executed to reach desired results.

Materials and Methods

Experimental Set-Up

The laser corroded layer removing processes were carried out by using a Ti: Sapphire ultrafast pulsed laser system which provides ~90 fs laser pulses with up to a 3.5 mJ energy per pulse at 1-3 kHz repetition rate (Quantronix, Integra-C-3.5, NY, USA) pumped by a Kerr-Lens mode-locked Ti:Sapphire oscillator laser (Quantronix, Ti-Light, NY, USA) (with 330 mW pulse power). Ti:Light oscillator laser produces laser pulses at ~90 fs in duration with a 85 MHz repetition rate with ~3 nJ energy per pulse at a fundamental wavelength of 800 nm.

The laser output was controlled by using an oscilloscope (LeCroy Corporation, WaveRunner 64 Xi, NY, USA) and a PC system. Historical coin were placed at the focal point of the laser beam using a micromachining system (Quantronix, Q-Mark, USA) to scan them as shown in figure 1.

Fs laser ablation were performed on historical metal coin using different laser intensities from 1.96 $\times 10^{13}$ W/cm^2 to 9.82 x 10^{14} W/cm^2 in atmospheric conditions. Historical coin was placed the bottom of micromachining unit shown in figure 1. Fs laser ablation processes were carried out at the room temperature conditions.

Images of the surface were taken using optic microscope (Ceti, light microscope) before and after fs laser cleaning processes and a Scanning Electron Microscope (SEM) (Zeiss Evo Ls 10, Cambridge U.K.) images and - Energy Dispersive X-ray (EDX) spectra have been obtained to compare either image & compositions of surfaces before or after corrosion removing process. To determine the laser optimum parameters of the laser for ablation process, such as laser repetition rate, laser wavelength and laser pulse duration which were kept constant and laser pulse power was changed to observe the effect of laser intensity on the removal of corroded layer on the material surface.

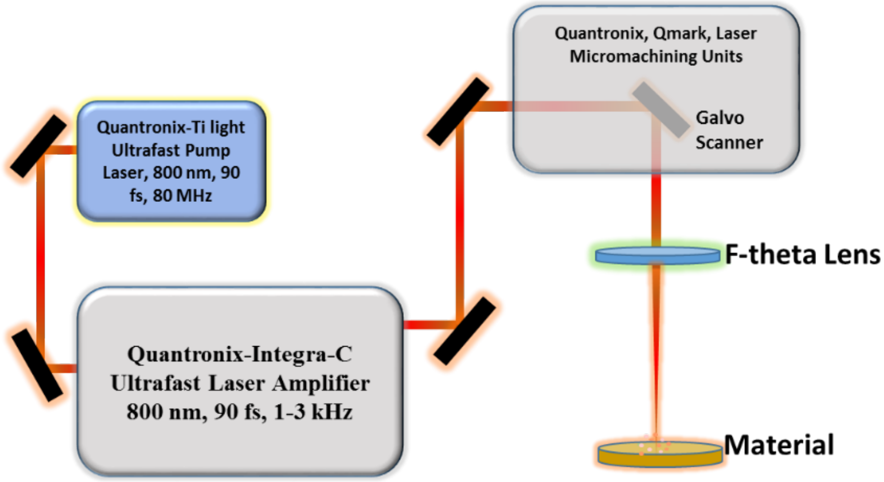


Figure 1. The schematic representation of fs laser ablation unit for cleaning process

Archaeological Characteristics of the Material

The coin used in this study shown in figure 2 belongs to Bythinia Region. Bythinia includes the center of Nicaea (modern Iznik) and the eastern and southern parts of the Marmara Sea (Propontis). The coin here is made of bronze and it was used during the Roman Empire Period in the 2nd century A.D. The front of the coin cannot be defined due to intense corrosion. On the reverse, there is a temple with eight rows of columns (octasylos) on a three-stepped podium. In addition, KOINON BEIYYIIAC, which is the meaning BITYNIA UNION, is written here., the used coin in this paper, which is the subject of the study. Itwas used as a common commercial tool in more than one city. The coin, with a diameter of 33 mm and a weight of 26 grams, is like the coins of the Antonine Dynasty (98-193 A.D.) when compared to other examples found before. The closest examples here are the coins belonging to Trajan (98-117 AD), Hadrianus (117-138 AD) and Sabina (AD 117-136) who was wife of Hadrianus. When evaluated according to its weight and diameter, the coin is like the coins which is the front of portrait of Hadrian. Nicomedia, the capital of the Kingdom of Bythinia, also minted coins (koinon) in the reign of Hadrian, starting especially in the reign of Claudius (Waddington et al., 1912).

Figure 2. Front (left) and back sides of the laser ablated coin

Metal Object

Laser parameters were applied on a surface area of 1 mm x 1 mm square. Spot size of laser beam used was 8mm. The laser wavelength used for all experimental works was 800 nm and laser beam were focused on historical materials using a fully computer-controlled micromachining system which has an 11 cm focal point f-theta lens. In laser micromachining unit, laser marking speed and skip speed were set at 10 mm/s and 125 mm/s respectively, and cleaning process was repeated from 5 to 10 repetition times to obtain a non-corroded surface. The laser fluence values used to perform to clean coin surface from 5.55 x 10^2 J/ cm^2 to 2.77 x 10^2 J/ cm^2.

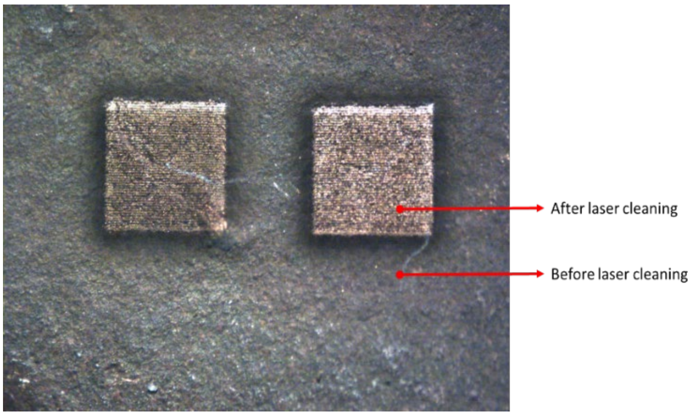


Figure 3. Photos shows the diameter of used coin and microscope images were recorded from ancient coin which is obtained from coin surface before and after laser cleaning.

Figure 3 was recorded by using optical microscope (right) and taken photo (left) to display the used coin diameter which has 3 cm. Some parts of the ancient coin contained copper at the same time the relief layer was quite worn.

Results and Discussion

One of the most important types of the archaeological findings is metal objects including coins. The most important problems on the coins and other metal findings are corrosion on their surfaces due to their burial-preservation conditions (Abdel-Karim & El-Shamy, 2022; Prokuratov et al., 2020). However, coins are not only commercial value, but they also provide important information about the age when they belong to. The depiction of the god or emperor on the coin contains very important information about the management of the age.

In this study, we have cleaned the surface of coin using 10 mW, 20 mW, 30 mW, 40 mW, 50 mW, 80 mW, 100 mW, 200 mW, 300 mW and 500 mW laser powers and changing the repetition of laser applications from 5 to 10 times shown in figure 4. Laser power dependence gives a pioneering information for conservation of art materials to take optimum parameters removing processes. It is an important concept to establish an optimum fs laser condition in order to spread the use of fs laser practically compared to other pulse duration laser types. One of the important points is high power laser conditions (≥200 mW) gives quite effective results in removing of corrosion layers on metal surfaces.

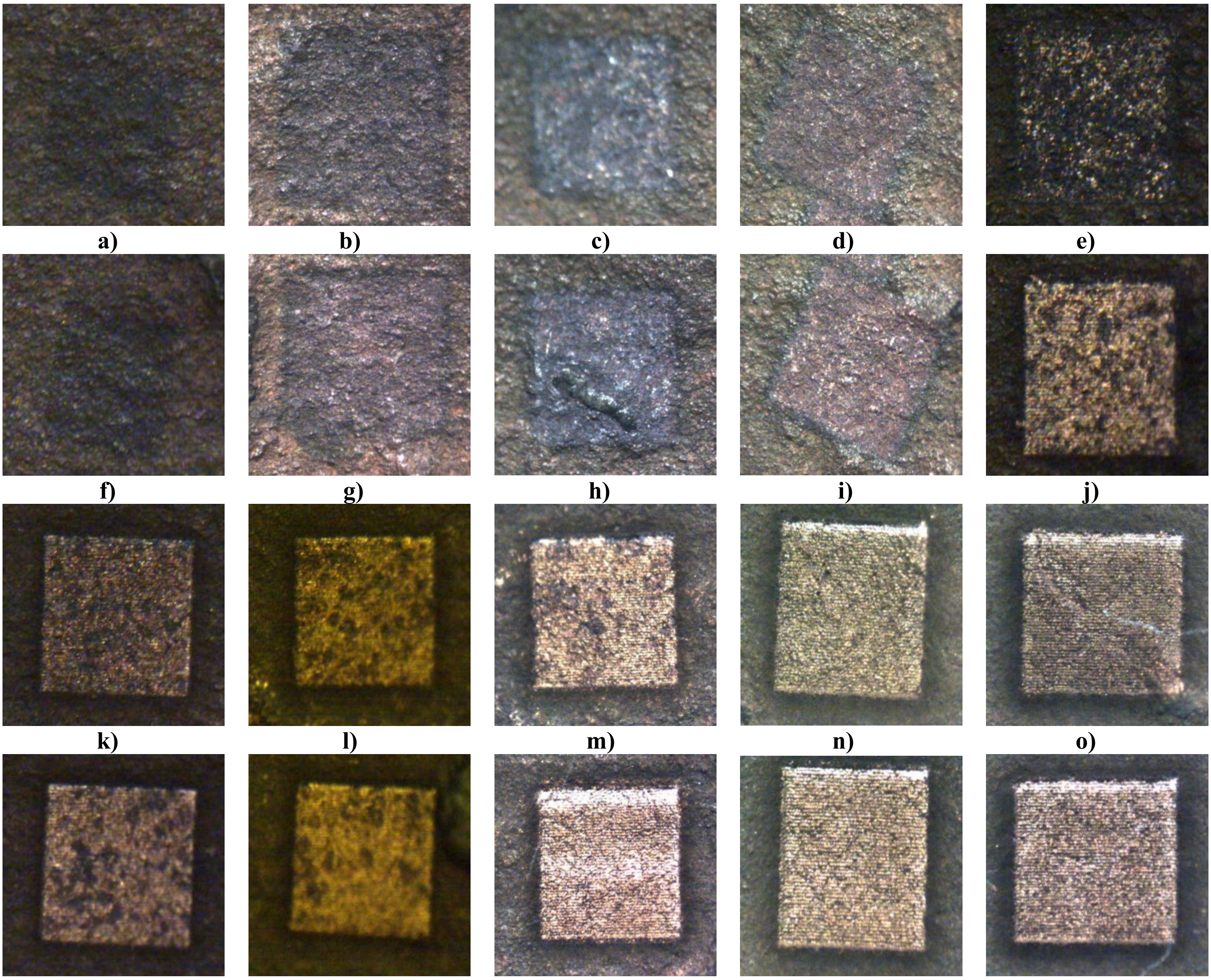
SEM- EDX results

The SEM and SEM-EDX results are shown in the figure 5 before and after the low power removing corrosion processing (10mW- 5 repetition) and high-power removing corrosion processing (500 mW-10 repetition) were applied.

Figure 5 shows details of experimental work carried out in this study. The SEM-EDX results are given according to coin's copper, oxygen, carbon, chlorine, silicon, tin, sulfur, zinc and aluminium elements due to the corroded layer at low laser power of about 10 mW (1,96 x10^{13} W/cm^2) and low repetition times (5 times). It was observed from the EDX graphs obtained that copper-zinc alloy on the original surface was high for the laser density of 9.82 x 10^{14} W / cm^2 (500 mW) (figure 5 (c)). Increasing ratio of copper and zinc in figure 5(c) shows the result as an indication that the coin is made of copper-zinc alloy.

An interpretation of the surface before laser cleaning application is given with the surface composition of coin in figure 5a, and it can be seen from SEM-EDX report in figure that a number of elements such as oxygen, carbon, calcium, silicone elements have intensities much higher than the copper and zinc ratios which the coin consists of copper zinc alloys. This is a strong indication that there are several materials coming from corroded layer before laser cleaning was applied.

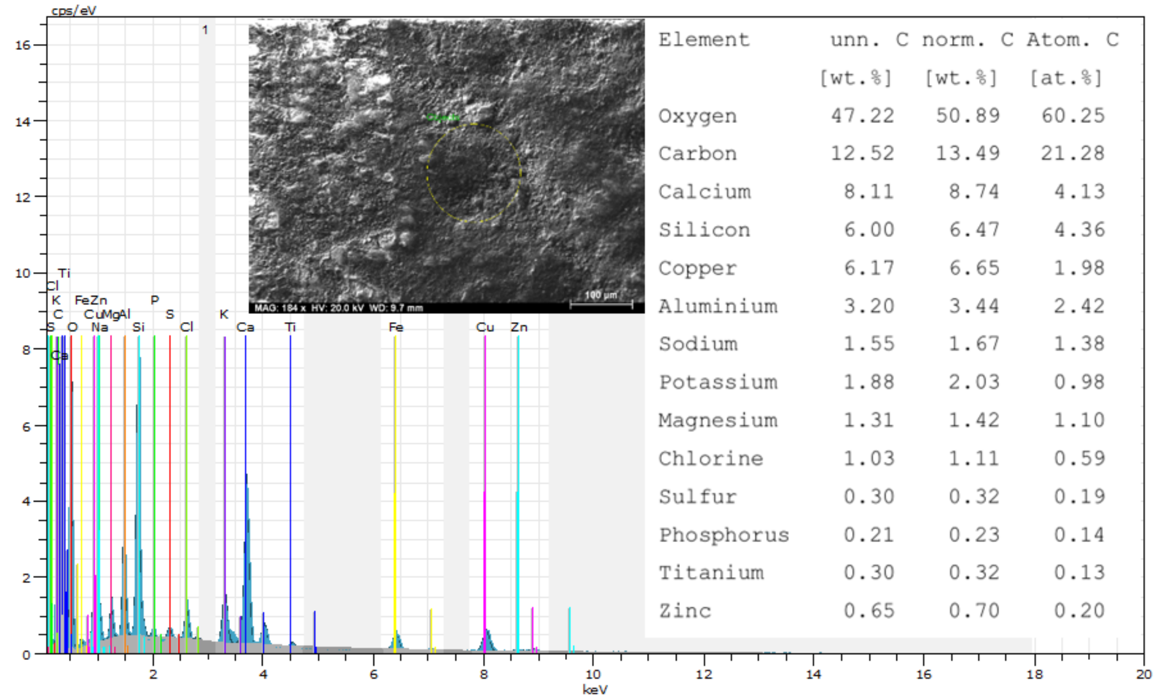
Figure 5(b) shows the results after laser cleaning process was applied to the surface. The obtained results show that fs laser is successfully used to remove the corroded layer from the coin surface due to decreases in intensities of elements from the corroded layer compared to that of elements of copper and zinc from the coin which is made of. The cleaning process was carried out using 10mW laser power and cleaning process was performed by 5 times laser applications. When comparing the data presented in Figure 5(a) with that in Figure 5(b), it can clearly be seen that the corrosion layer is cleaned successfully. The peaks given in in Figure 5(c) shows that the results are even better due to the intensities of oxygen and carbon peaks due to the SEM-EDX graphs.



p) r) s) t) u)

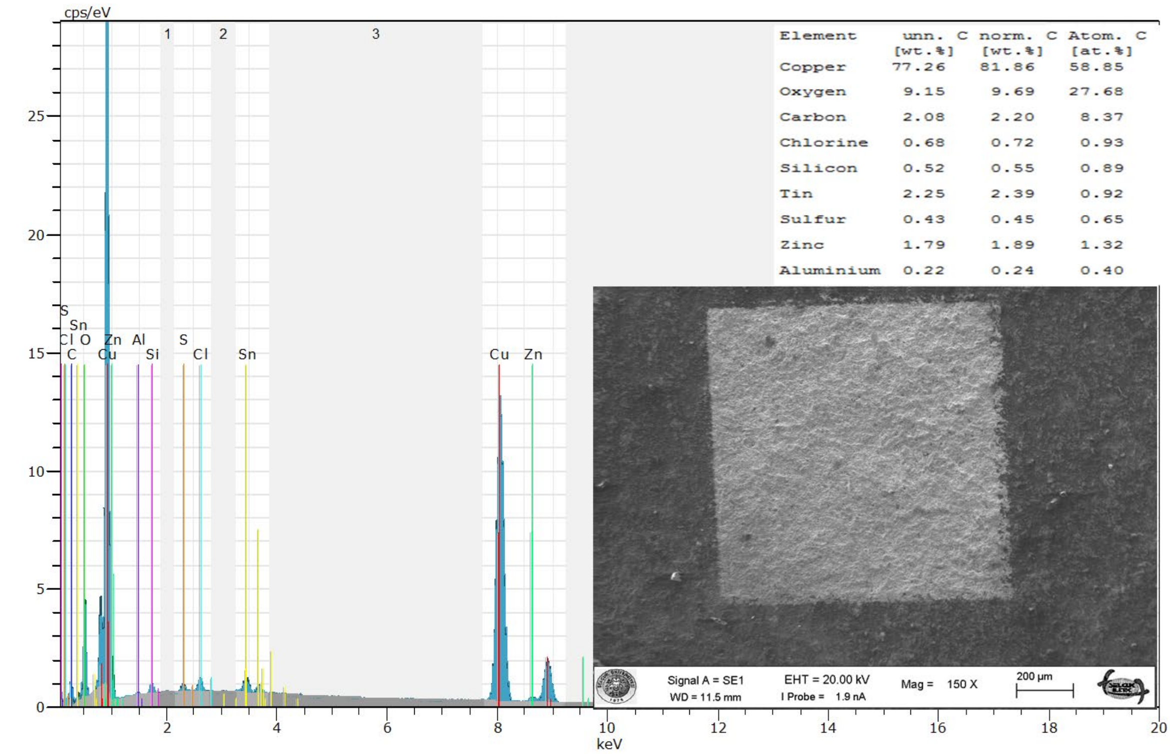
Figure 4. Optical microscopic images are obtained from fs laser-historical coin interactions depending on laser power-repetition times as a) 10 mW-5 repetitions, b) 20 mW-5 repetitions, c) 30 mW-5 repetitions, d) 40 mW-5 repetitions, e) 50 mW-5 repetitions, f) 10 mW-10 repetitions, g)20 mW-10 repetitions, h)30 mW- 10 repetitions, i)40 mW-10 repetitions, j)50 mW-10 repetitions, k)80 mW-5 repetitions, l) 100 mW-5 repetitions, m) 200 mW-5 repetitions, n) 300 mW-5 repetitions, o) 500 mW- 5 repetitions, p)80 mW-10 repetitions, r)100 mW-10 repetitions, s) 200 mW-10 repetitions, t)300 mW-10 repetitions, u) 500 mW-10 repetitions.

In historical works, cultural heritage and artworks require careful cleaning without damaging the original surface of materials which they are mostly exposed to corrosion. Fs laser-based corrosion removal is known as an important technology cracks or scratches to deterioration of the structure of the material. Especially, the laser pulse duration is an effective parameter for the heat transfer or non-heat transfer during laser-materials interaction and cleaning process. When the laser interacts with the material in femtosecond(10^{-15}s) time scale, this time is shorter (10^{-8}s) than the interaction time of the atoms with each other and the negative effects such as burn, or crack disappear. Using fs laser is an advantageous to compare the other laser types due to pulse duration.



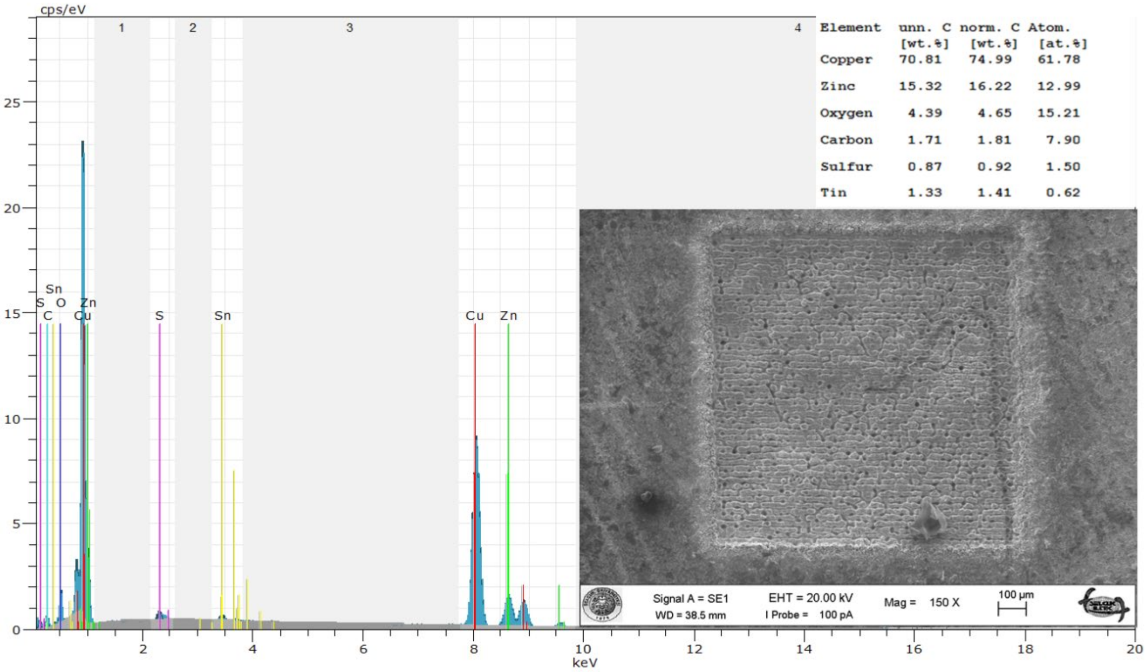
Element	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]
Oxygen	47.22	50.89	60.25
Carbon	12.52	13.49	21.28
Calcium	8.11	8.74	4.13
Silicon	6.00	6.47	4.36
Copper	6.17	6.65	1.98
Aluminium	3.20	3.44	2.42
Sodium	1.55	1.67	1.38
Potassium	1.88	2.03	0.98
Magnesium	1.31	1.42	1.10
Chlorine	1.03	1.11	0.59
Sulfur	0.30	0.32	0.19
Phosphorus	0.21	0.23	0.14
Titanium	0.30	0.32	0.13
Zinc	0.65	0.70	0.20

(a)



Element	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]
Copper	77.26	81.86	58.85
Oxygen	9.15	9.69	27.68
Carbon	2.08	2.20	8.37
Chlorine	0.68	0.72	0.93
Silicon	0.52	0.55	0.89
Tin	2.25	2.39	0.92
Sulfur	0.43	0.45	0.65
Zinc	1.79	1.89	1.32
Aluminium	0.22	0.24	0.40

(b)



(c)

Figure 5. SEM images, SEM-EDX graphs and SEM-EDX reports are shown in (a) Before laser cleaning to control coin surface (b)10mW laser power with 5 repetition times (c) 500 mW laser power with 10 repetition times.

Conclusion

The reported fs laser cleaning work in this study was done using 90 fs laser pulses in duration at 800 nm laser wavelength with no heat transfer to the sample. The most important advantage of the fs laser is that all cleaning processes can be examined in laboratory conditions, which reduce the undesired effects of different types of corrosion depending on their location, climate, and water factors.

Careful choice and investigation of optimal laser parameters must be identified for ablation conditions in the arts cleaning material removal studies (Gamaly et al., 2002; Liu et al., 1997). Low level laser power level (≤10 mW) is not to proper for cleaning comparing to high level laser powers (≥200 mW). One of the important points is high power laser conditions (≥200 mW) gives quite effective results in removing of corrosion layers on metal surfaces. Moreover, changing the repetitions from 5 to 10 times means shortening the ablation time and the cleaning process. SEM-EDX results show that copper- zinc alloy percentage is greater for 500 mW-10 repetitions times because of surface of coin becomes more cleaned and corrosion-free surface.

Optimized laser parameters for marking speed, skip speed, repetition times are ideal for copper-zinc alloy materials cleaning, but some ancient coin includes soft relief layers. It would be more appropriate to use low laser power and repetition times for the ancient coins with the relief layer for further applications.

The best method applied on archaeological artifacts is mechanical cleaning without using chemicals. At the same time, it has the advantage of minimizing the risk of any layer or corrosion formation on the work because it is a recyclable work. For this reason, it is one of the most successful techniques among conservation methods, as it offers the opportunity to analyze again in the future.

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Note: The permission document to allow us to remove of corrosion layer on ancient coin samples have been got from Ministry of Culture of Republic of Turkey and they have been given back to museum after cleaning process.

Conflict of Interest Statement: On behalf of all authors, the corresponding author states that there is no conflict of interest.

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