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Analysis of ceramics surface modification induced by pulsed laser treatment

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Abstract

This paper presents the effects of laser light irradiation on the surface of ceramics dating from archaeological site Stubline (Obrenovac, Belgrade), Serbia. Two different pulsed lasers: TEA CO_2 (10.6 µm wavelength, pulse duration t_p = 100 ns) and Nd:YAG (wavelengths 1064 nm and 532 nm, t_p = 150 ps) have been used for surfaces treatment. Laser irradiation fluence was in the range of 1–20 J/cm^2. Ceramics surface modifications induced by pulsed laser treatment were examined by scanning electron microscope, SEM, and the composition with energy dispersive X-ray, EDX, analysis. The tests were performed in order to obtain as much as possible information about the appropriate choice of materials and techniques for the further conservation and restoration of these items. The second objective was to determine the surface modifications induced by pulsed laser treatment above damage threshold (a safe cleaning laser fluence), as an important parameter in the use of lasers for the cleaning of cultural ceramic items.

Keywords: *Neolithic ceramics, laser processing, surface properties, structural characterization*

I. Introduction

Protection of cultural heritage is based on the application of new technologies, methods and materials in diagnostic and conservation process of artefacts. Contemporary laser methods are dominant in diagnosing the state, identification and in protection of the cultural heritage objects.

Ceramic artefacts have an important role in archaeology; they are among the most common artefacts found at an archaeological site. Ceramics have had an important part of human life throughout the history. It is an inorganic, non-metallic, crystalline material. Ceramic objects are made up of a mixture of natural materials that are, by a variety of processes, transformed to a solid, brittle substance with high thermal resistance, high hardness and chemical stability. The earliest ceramics were pottery [1] objects or 27000 year old figurines made from clay and hardened in fire. In the past, ceramic is used for decorative or practical objects [2]. A detailed knowledge of the ancient ceramics characteristics and their production methods is important for solving problems of authentication, conservation and for classification the items in historical period and in a geographical region. Thus, Petrović *et al.* [3] pointed out the importance of correct methodology for the procedures of the restoration. They examined clay products from the fortress in Bač and based on the used methods, mineral composition, temperature and regime of firing and textural properties of the examined materials were determined.

The study of the laser radiation impacts on the surface of ceramics is significant in terms of lasers application in diagnostic, cleaning, and other methods. Irrespective of whether it is used for diagnostics or for cleaning, laser light must have the parameters selected in such a way that the surface of samples (artefacts) of cultural heritage remains unchanged [4–10].

Ceramics and lasers impact on them are the subjects of many scientific papers. Sartinska *et al.* [6] presented results of surface modification of materials with different structures by exposure to nanosecond pulsed diode-pumped solid state and YAG laser. The modified surface layers were examined by scanning electron microscopy to reveal the formation of new nanostructures and new morphologies. Another very interesting paper [11] de-

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scribes laser application in strengthening large ceramic structures with damages due to cracks which occur over time due to various reasons. The modification of ceramic surfaces by directional laser melting can eliminate surface defects and thus improve the ceramics mechanical performance, as long as one prevents the formation of cracks [11]. Thus, interaction of ruby laser beam with Neolithic ceramics from Stubline, Serbia was investigated by Ristic *et al.* [12].

Influence of laser irradiation on ceramic artefacts is also a very attractive research field, because the potential of laser techniques in conservation has needed a long development period to be fully applied. The possibility to achieve a very precise and selective removal of deposits requires series of interdisciplinary studies. A suitable choice of the laser types and of the operating parameters could optimize the cleaning results, avoiding side effects. An extensive validation carried out on a number of renowned masterpieces has definitely spread the interest of the conservation community for laser techniques in all over world [2,4].

Archaeological site Stubline - Neolithic period

Forty kilometres away from Belgrade, in the environs of Obrenovac, in the village of Stubline, there are the finds of a major Neolithic settlement, which is assumed to cover an area of around 16 hectares. The last stage of the life in that settlement belongs to the period of the Late Neolithic period, or to the very end of the Vinča culture, the greatest prehistoric culture of Europe and one of the highest developed cultures of its time. It was developed from around 5250 to about 4500 B.C. as an autochthonous Balkan culture that emanated from the transformation of the previous, Neolithic-Starčevo culture, which had had the cultural continuity with an even older, Mesolithic culture of Lepenski Vir [13].

The first finds appeared at the site of Stubline at a depth of just 30 cm, and already the initial investigations at the settlement in Crkvine yielded an abundance of movable finds, such as pieces of pavements, bowls, utensils, amphoras, weights for weaver's frames, and by all means the most interesting finds, 46 Neolithic figurines [14–16]. Two pieces of Neolithic ceramics from Stubline were used in the presented study.

Laser-ceramic interaction

Absorption, reflection, refraction, transmission, and scattering are the different physical phenomena that take place when the laser beam is incident on the ceramic surface. The majority of the energy is absorbed and this absorption depends on the wavelength and spectral absorptivity characteristics of the material. The laser absorbed energy, converted into heat, conducts into the material according to Fourier's second law of heat transfer, and simultaneously radiates and convects from the surface. The sample surface temperature is variable during laser irradiation. It depends of variations in thermal conductivity and specific heat, as a function of temperature. The main processes are mathematically described in literature [17].

The interaction of laser beams with materials is a complex phenomenon that depends on many factors [18]. Laser ablation is process, consisting of optical, photo thermal, photo acoustic and photo mechanical phenomena, which depend on the parameters of the laser beam and materials. The energy density of the laser beam, the time of irradiation or pulse length, the wavelength, and the energy distribution within the beam are related to the laser characteristics. The reflection and absorption coefficients, surface shape, homogeneity, temperature coefficient, melting point, and boiling point are related to the material of the object.

Laser based techniques are essentially thermal processes. In these processes absorption of a large number of photons heats the material and performs surface modification, locally melting and remelting of the substrate. The continual work lasers with infrared wavelength are used for photo thermal ablation. This ablation of material is combination of evaporation and melts expulsion. In laser ablation, time is very short for significant heat conduction through the substrate. The rapid increase of thermal energy is only in the optical absorption depth, where the melting and vaporization of the material and the formation of dense plasma can occur.

Laser spallation is a removal process that is often used for cleaning of ceramics. It utilizes laser-induced thermal stress to fracture the contamination layers into small fragments before melting of the ceramics occurs. High intensity laser energy and short time pulses applied on a ceramics sample with very low thermal conductivity, concentrates locally on the surface layers and causes the local temperature to increase instantaneously [19]. The maximum temperature just below the melting temperature can be obtained by carefully controlling the laser parameters. This results in a local thermal stress in subsurface that is enough to spall the contamination layer.

"Cold" ablation is an attractive mechanism in art conservation. There is no (or little) attendant heating effect. The highly energetic ultraviolet wavelength lasers, such as excimer, are capable of providing enough energy to directly break C-H bonds in organic materials and resulting cold ablation.

The aim of this paper is to present the results concerning the usage of short laser pulses (nano- and picosecond) for surface modification and determination of chemical composition of Neolithic ceramics, which are important for improving the cleaning techniques and avoiding cracks and inhomogeneities around the interaction zone.

II. Experimental

2.1. Description of ceramic samples

Two pieces of Neolithic ceramics from Stubline (IG 203 A and IG 203 B) were used in the presented study.

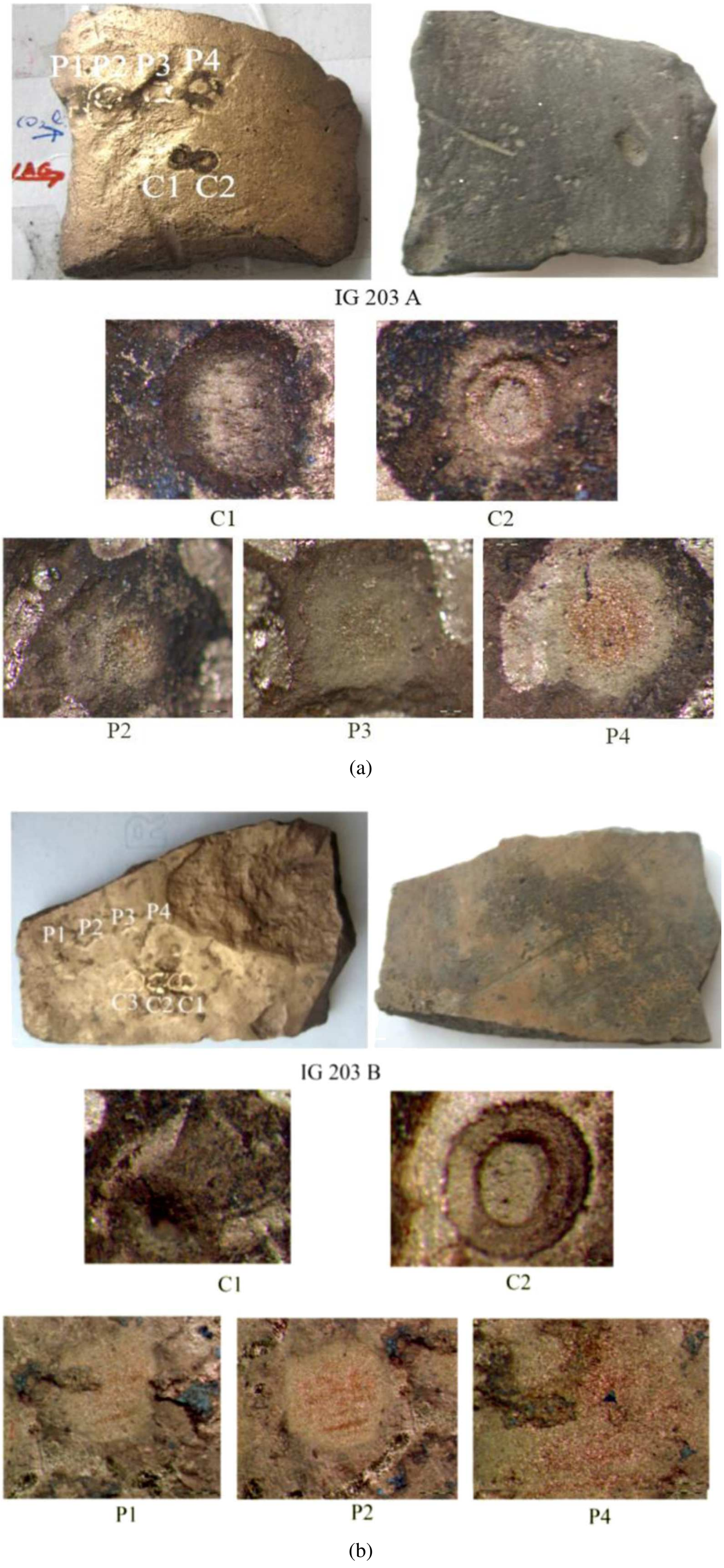


Figure 1. Appearance of Neolithic ceramics with laser treated zones: a) IG 203 A and b) IG 203 B (zones P1-P4 were irradiated with TEA CO_2 laser and zones C1-C2 were irradiated with Nd:YAG laser)

The pieces were irradiated with Nd:YAG and TEA CO_2 pulsed lasers. Appearance of the pieces with laser treated zones is presented in Fig. 1. The front side surfaces are sputtered with gold and back ones are with original, no prepared surfaces. The surfaces of the samples are not glazed. The sample IG 203 A has a dark grey colour, and IG 203 B is brown. The samples were carefully cleaned of the clay layers and washed with water, before laser cleaning.

2.2. Lasers

The samples were irradiated by pulsed laser beam focused using ZnSe (TEA CO_2 laser) and quartz lens (Nd:YAG laser) of 14 and 10 cm focal length, respectively. Laser beams were directed perpendicularly to the specimen. All irradiations were performed in atmospheric conditions at the pressure of 1013 mbar, temperature of 293 K and standard relative humidity. Laser repetition rate was in the interval from 20 to 1000 Hz. During irradiation process lasers were running in the multimode or near-fundamental mode regime.

The used lasers are commercial versions. TEA CO_2 laser system was developed at the VINCA Institute [20], and it is a miniature, compact system with the wavelength of 10.6 μm. Optical pulse had a gain switched peak followed by a slowly decaying tail. Full width at a half maximum (FWHM) of the peak is about 100 ns, while the tail duration is ~2 μs. Output multimode pulse energy was up to 200 mJ. The Nd:YAG laser is also commercial system developed at EKSPLA Company, model SL212/SH/FH, with the following characteristics: wavelengths 1064 or 532 nm; optical pulse duration 150 ps (FWHM); output pulse energy up to 150 (1064 nm) and 50 mJ (532 nm).

2.3. Sample characterization

Scanning electron microscopy (SEM) and energy dispersive X-ray spectrometry (EDX) were performed for microstructural and microchemical characterization. The ceramics surface and cross section microstructures and micro-morphology were monitored by optical microscope SZX10 OLYMPUS microscope, too. Prior to examination the specimens by JEOL JSM-6610LV scanning electron microscope, surface was sputtered with gold. An acceleration voltage of 20 kV was applied and the sample was coated with a thin layer of gold 20 nm thick. SEM was connected with INCA350 energy-dispersion spectroscope (EDX). The EDX is used for analysis of the sample composition and for determination the changes in the material composition of the irradiated zones and ablated material.

III. Results and discussion

Macroscopic, visual analysis of the tested samples of ceramics objects (Fig. 1) shows that the applied laser fluences caused more or less removal of deposits. The energy density, fluences of the laser beam, the wavelength, and the number of pulses applied on the marked zones (Fig. 1) are presented in Table 1.

Table 1. Laser experimental parameters

Zone - laser type	Energy density [J/cm^2]	Wavelength, λ [nm]	Number of pulses, n
IG203A			
C1 - Nd:YAG	1.2	1064	200
C2 - Nd:YAG	3.3	1064	200
P1 - CO_2	7.0	10.6×10^3	50
P2 - CO_2	7.0	10.6×10^3	200
P3 - CO_2	4.0	10.6×10^3	50
P4 - CO_2	4.0	10.6×10^3	200
IG203B			
C1 - Nd:YAG	20	1064	50
C2 - Nd:YAG	20	1064	200
C3 - Nd:YAG	20	536	200
P1 - CO_2	1.0	10.6×10^3	50
P2 - CO_2	1.0	10.6×10^3	200
P3 - CO_2	1.1	10.6×10^3	50
P4 - CO_2	1.1	10.6×10^3	200

SEM and EDX analysis of sample IG 203 A

Visual analysis of the tested IG 203 A sample shows that application of Nd:YAG and TEA CO_2 laser fluences caused obvious surface degradation (Figs. 2 and 3). The zone irradiated by a laser beam has two sub-zones: the central in which melting of the surface layer is occurred, and the peripheral zone or area with sediment molten matters (Figs. 2a,c).

The irradiated zones C1 and C2, obtained with Nd:YAG laser (λ = 1064 nm), are with well-defined shape, what is typical for lasers with short pulses (pulse duration 150 ps). Laser fluence, used for irradiation of zone C1, was 1.2 J/cm^2 and number of the pulses was 200. The zone C2 (Fig. 2b) shows that laser beam, with higher energy density 3.3 J/cm^2 (200 pulses), penetrated deeply into the ceramic body, and that there is more of molten material which forms the white zone as a sediment (Fig. 2b, zone C2). Laser remelting process is the fundamental process in which the substrate surface is melted locally by the laser beam and solidifies. This modification can be used to eliminate surface defects and to improve the ceramics mechanical performance. Table 2 shows that there are no significant changes of chemical constitution of material in the irradiated zones versus laser fluences and number of laser pulses. For the higher energies and same number of the laser pulses, the chemical composition in the center of irradiated zone shows the same proportion of O, Mg, Ca, Fe and Ti, and a smaller fraction of Al and K. TEA CO_2 laser beam also causes clearly visible degradation of the IG 203 A sample surface, but with not well defined shape and more expressed melting process (Fig. 3). Thus, TEA CO_2 laser irradiation produced crate on the surface typical for thermal ablation. The interaction of CO_2 laser beam and ceramic artefact is essen-

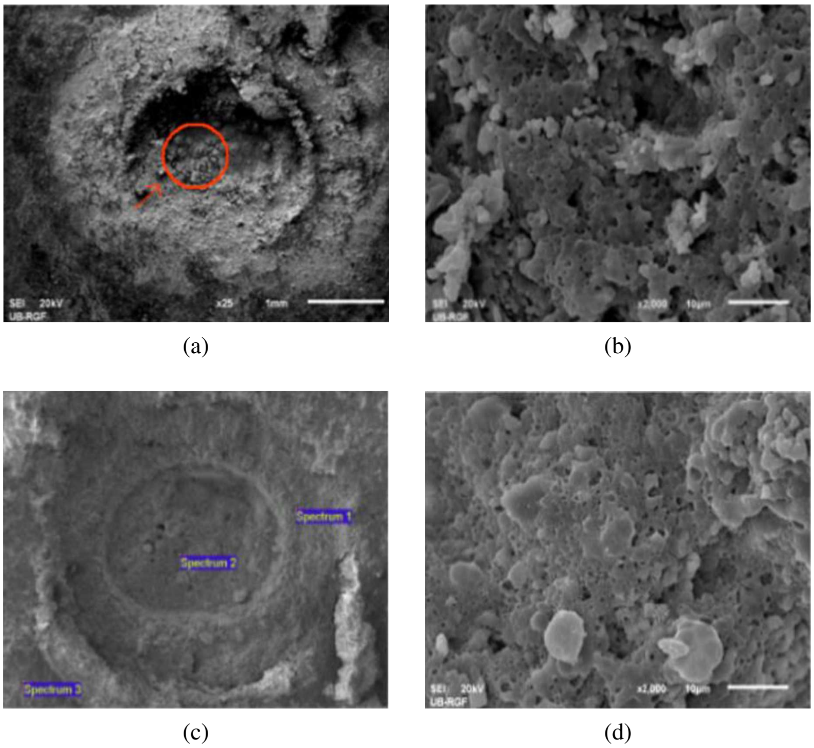


Figure 2. SEM micrographs of irradiated surface of IG 203 A sample with Nd:YAG laser: a) zone C1 (low magnification), b) zone C1 (high magnification), c) zone C2 (low magnification) and d) zone C2 (high magnification)

Table 2. EDX date for zones C1 and C2 on sample IG 203 A irradiated with Nd:YAG laser (all results are in wt.%)

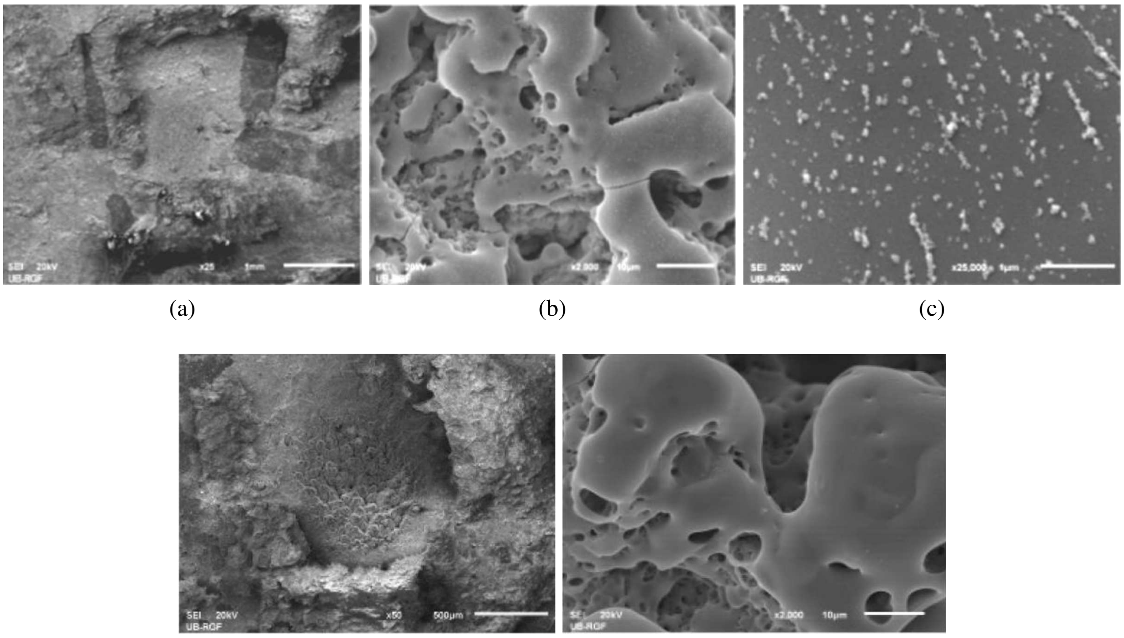
Spectrum	O	Mg	Al	Si	K	Ca	Ti	Fe
IG203A - Nd:YAG laser, zone C1								
non-irradiated surface	43.5	1.6	9.6	25.8	3.9	5.7		9.9
peripheral area	51.5	1.6	9.5	23.1	3.0	1.9	0.6	8.8
central zone	51.2	1.5	9.5	23.2	2.7	4.4	0.7	6.9
IG203A - Nd:YAG laser, zone C2								
non-irradiated surface	46.4	1.6	8.5	28.4	2.3	4.6	0.6	7.7
peripheral area	43.3	1.7	12.5	25.7	4.2	3.7	0.6	8.3
central zone	51.6	1.5	8.5	27.0	2.4	2.2		6.8

tially thermal processes. In these processes absorption of a large number of photons heats the material and performs surface modification, locally melting and remelting of the substrate (Fig. 3c). When CO_2 laser is used, typical cones were not formed after 50 pulses (the zone P1, Fig. 3a), but they can be easily seen on SEM micrograph of the IG 203 A surface irradiated with 200 pulses having the fluence of $\Phi = 7$ J/cm^2 (the zone P2, Fig. 3d). The chemical analysis of the irradiated zones P1 and P2 is shown in Table 3. It can be seen (Table 3) that the increased number of pulses (with the same energy of CO_2 laser beams) gives the changes in the chemical composition as follows: decrease K and Ca in the centre of the zone and increase portion of Fe. The other element proportions are without significant differences in the centre of zones related to the non-irradiated surface.

SEM and EDX analysis of sample IG 203 B

The sample IG 203 B, which belongs also to the archaeological site Crkvine, was prepared, for testing, in the same way as the previous one. For irradiation of the sample IG 203 B high fluence of Nd:YAG laser was used, and SEM micrographs of the irradiated zones were presented on Fig. 4. The zone C2, irradiated with a wavelength of $\lambda = 1064$ nm, is much larger than the zone C3 obtained with the same number of pulses, but lower wavelength, $\lambda = 532$ nm (Figs. 4b,c). It is, probably, result of different absorption coefficient of chemical constituents. The SEM micrographs of the zones irradiated by Nd:YAG laser with the same fluences and different number of pulses (the zones C1 and C2 obtained with 50 and 200 pulses, respectively) are presented in Figs. 4a and 4b. It can be seen that the laser beam penetrated deeply into the ceramic body when higher number of pulses was used.

The SEM micrographs of zones irradiated by CO_2 laser with the same fluences and different number of pulses are presented in Fig. 5. Like in the case of the sample IG 203 A, CO_2 laser beam causes melting of the surface layers of the sample IG 203 B without the for-



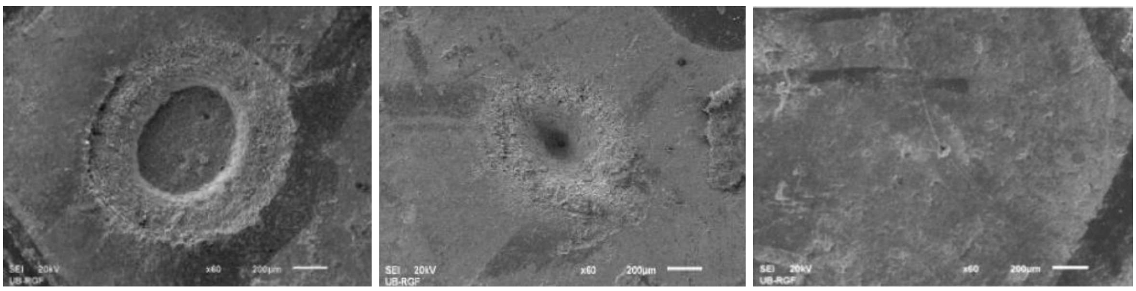
(a) (b) (c)

(d) (e)

Figure 3. SEM micrographs of irradiated surface of IG 203 A sample with CO_2 laser: a) zone P1(low magnification), b) zone P1 (high magnification), c) non-irradiate surface close to zone P1, d) zone P2 (low magnification) and e) zone P2 (high magnification)

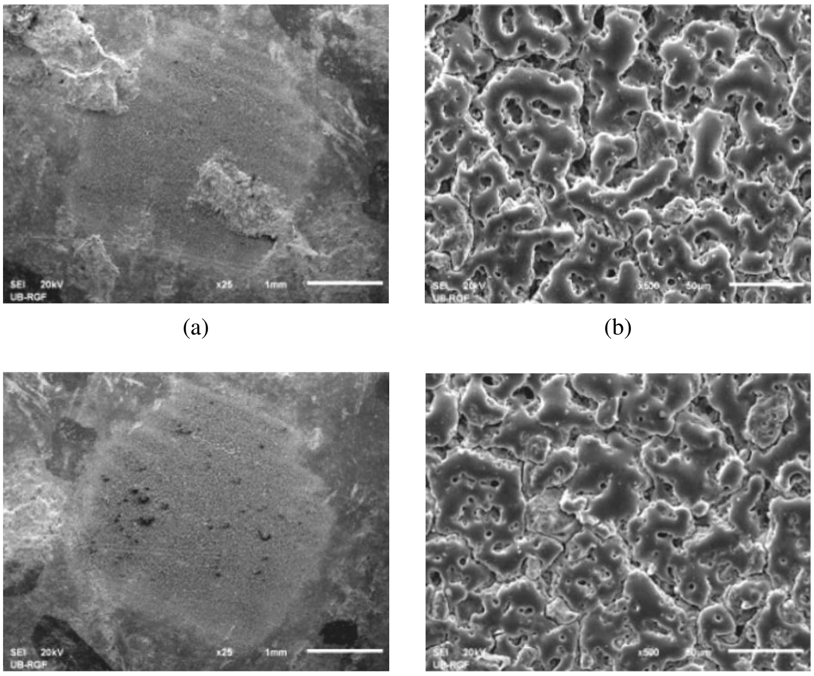
Table 3. EDX date for zone P1 and P2 on sample IG 203 A irradiated with CO_2 laser (all results are in wt.%)

Spectrum	O	Mg	Al	Si	K	Ca	Ti	Fe
IG203A - CO_2 laser, zone P1								
non-irradiated surface	37.7	1.7	10.9	26.5	4.7	7.1	0.8	10.6
peripheral area	38.5	1.8	8.7	30.4	4.2	7.6	0.7	8.1
central zone	42.0	1.8	12.1	22.3	3.5	6.6	0.4	11.2
IG203A - CO_2 laser, zone P2								
non-irradiated surface	40.6	1.0	10.9	33.0	3.2	4.7		5.7
peripheral area	41.4	1.7	11.1	26.0	2.4	3.9	0.8	12.6
central zone	43.4	1.8	9.8	19.1	1.4	2.3		22.1



(a) (b) (c)

Figure 4. SEM micrographs of irradiated surface of IG 203 B sample with Nd:YAG laser: a) zone C1, b) zone C2 and c) zone C3



(a) (b) (c) (d)

Figure 5. SEM micrographs of irradiated surface of IG 203 B sample with CO_2 laser: a) zone P1 (low magnification), b) zone P1 (high magnification), c) zone P2 (low magnification) and d) zone P2 (high magnification)

Table 4. EDX date for zone C1, C2 and C3 on sample IG 203 B irradiated with Nd:YAG laser (all results are in wt.%)

Spectrum	O	Mg	Al	Si	K	Ca	Ti	Fe
IG203B - Nd:YAG laser, zone C1								
non-irradiated surface	46.15	0.91	9.23	28.03	4.41	4.65	0.37	5.60
peripheral area	46.96	0.71	9.25	28.96	3.35	4.96	0.69	4.52
central zone	46.94	0.81	9.45	28.40	2.91	5.00	1.11	5.38
IG203B - Nd:YAG laser, zone C2								
non-irradiated surface	46.56	0.92	9.52	28.23	4.42	4.93	0.49	4.93
central zone	46.36	0.92	9.35	27.91	4.03	5.28	0.50	4.93
IG203B - Nd:YAG laser, zone C3								
non-irradiated surface	47.37	0.96	9.84	30.79	4.27	4.47	0	3.90
central zone	47.31	0.79	9.21	29.85	3.37	5.80	0	3.67

mation of cones typical for Nd:YAG laser. The mechanism of laser–IG 203 B sample interaction is the same as the mechanism for IG 203 A sample, and the irradiation effect are very similar.

The EDX analysis showed no significant difference in chemical composition of the samples IG 203 A and IG 203 B of Neolithic ceramics. The difference occurs only in content of Fe. The EDX analyses of sample in irradiated zones are given in Tables 4 and 5. The results for the sample IG 203B show that irradiation with Nd:YAG laser beams caused the changes in the chemical composition of surface as follows: the portion of O is the same in the non-irradiated and centre of irradiated zones C1, C2 and C3. Portion of K decreased in the centre of the zones and amount of Ca increased. The content of other element are without significant differences in the centre of zones related to non-irradiated surface. The results of CO_2 laser irradiation of sample IG 203B show that there are the following changes in chemical composition: O and Si are present with the same content either in non or irradiated zones, portions of Mg, Ka and Fe slightly decrease, whereas contents of Al and Ti increase.

IV. Conclusions

The main aim of this research was investigation of chemical and morphological changes on the surface of the Neolitic ceramic samples (archaeological site of Stubline) irradiated by TEA CO_2 and Nd:YAG lasers. The effect of irradiation show that the different processes occurred during the laser treatment, melting, ablation and sedimentation.

The morphological analyses of the ceramics surface, after the CO_2 laser treatment, have shown the melting effects and formation of the conical structures. Diameter, height and distance between the cone peaks have a micrometric size. The ceramic surface became more roughness than the initial surface. The CO_2 laser irra-

Table 5. EDX date for zone P1 and P2 on sample IG 203 B irradiated with CO_2 laser (all results are in wt.%)

Spectrum	O	Mg	Al	Si	K	Ca	Ti	Fe
IG203B - CO_2 laser, zone P1								
non-irradiated surface	45.64	1.28	10.51	25.74	4.63	5.35	0.39	6.47
peripheral area	46.99	1.06	9.74	29.00	4.92	3.13	0.50	4.65
central zone	46.74	1.07	11.66	26.63	3.01	5.12	0.79	4.98
IG203B - CO_2 laser, zone P2								
non-irradiated surface	46.46	1.28	9.82	27.74	4.39	4.75	0.39	5.16
peripheral area	46.87	0.92	9.63	28.70	4.00	5.16	0.41	4.32
central zone	46.58	0.86	10.06	27.58	3.27	6.10	0.64	4.90

diation produced crate on the surface typical for thermal ablation and the morphological modifications depend on the laser fluences and number of pulses. The Nd:YAG laser irradiation, with fluence 1–20 J/cm^2, produces crates on the surface, typical for spalation mechanism. Picoseconds laser irradiation ejects material and makes fine defined form on the surface.

The tests by EDX were carried out on the surface treated by 50–200 laser impacts, with different wavelength, and on the non- irradiated surface. The EDX analysis confirmed that the chemical composition of the ceramic bodies is consisted of: Na_2O, MgO, Al_2O_3, K_2O, CaO, TiO_2, MnO and Fe_2O_3. The two samples have very similar chemical composition, it means that they belong to the same period and that are manufactured on the same, or the similar procedure.

The aim of EDX analysis of irradiated and non-irradiated zone was, above all, to determine the remove of sediments, based on differences in the chemical composition. The tests results, presented in this paper, can be used for the appropriate choice of materials for the further conservation and restoration of these items, too. The applied fluences were up to the damage threshold. Safe cleaning fluences (the damage threshold of the ceramic) have to be lower than 1 J/cm^2 for both of the applied lasers. On the base of results obtained in this research, the recommended fluence for cleaning the ceramics samples is about 0.5 J/cm^2 and repetition rate more than 200 pulses.

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