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XRF AND LIBS MEASURING ON METAL AND CERAMIC LASER-CLEANED SURFACES

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***Abstract* –The use of lasers in the conservation of artefacts plays an important role since its posibilities of safe, efficient and efective cleaning on complex surfaces and wide range of materials. This paper presents the results of the laser cleaning effects on ceramic medieval artefacts originated from archaeological sites from region of Tyre and Sidon, Lebanon and naturally tarnished brass plate (unknown origin). Nd:YAG and Er:Glass lasers were used to clean unwanted layers from artefact surface. Before these investigations, some preliminary analyses were conducted on the comparable contemporary samples. Effects on the laser irradiated zones were investigated by optical and SEM microscopy and EDX analysis. LIBS and XRF were used for the morphological and chemical analysis of laser radiation impact on the examined materials. Also surface's profile roughness and surface hardness were measured. Some parameters for successfully and safely cleaning of brass surface without degrading the surrounding material were determined.**

Keywords: laser cleaning, copper, ceramic, XRF, LIBS, SEM

I. INTRODUCTION

Implementing a laser treatment for cleaning the surface of artefacts requires the analyses of the material modifications from a topographic point of view as well as from the chemical and structural aspects [1].

Topography, chemical and structural composition of artefacts surfaces material before and after cleaning process indicates on cleaning effectiveness and can also be useful information for determination of artefacts provenience and degradation degree.

Spectroscopic techniques as Laser Induced Breakdown Spectroscopy (LIBS) and X-Ray Fluorescence (XRF) could be efficiently employed in determination of chemical and structural composition of artefacts [2,3].

K. Blagoev et al. [2] have used LIBS, XRF and XRD techniques for determining elemental composition of white clay ceramic tiles. M. F. Alberghina and her collegues [3] were compared the results obtained by LIBS measurements with X-Ray Fluorescence (XRF) ones, on calcareous and refractory materials coming from the Greek-Roman theater of Taormina. XRF investigations after laser treatments have been made on archaeological copper alloys [4] and on medival ceramic [5]. This methode can be used for authentication of archaeological objects and for various historical studies for validation of various hypotheses on the habits, commercial and cultural exchanges of old populations.

This paper present the results of lasers parameters optimization for effective and safely cleaning of ceramic and metal artifacts. In that purpose some preliminary investigation were conducted on contemporary ceramic and metal samples (figs 1a and 1b).

For the surface treatment there have been used Nd:YAG and Er:Glass lasers with short pulses duration (nanoseconds). During performed experiments, laser fluences and number of laser pulses were changed for each sample. Obtained results were compared with results of laser irradiation analyses on ceramic medival artefacts and naturaly tarnished brass plate (Fig. 1c and 1d). This comparison was conducted in order to determine whether there is a substantial difference in the cleaning effects and in order of determination of optimal laser cleaning parameters for similar materials in cultural heritage conservation.

I. METHODES AND EXPERIMENTS

A. Samples and applied lasers

For preliminary determination of optimal laser parameters for ceramic and metal samples safely cleaning, contemporary alumo-silicate ceramic tile with glazed and unglazed surfaces and silvered copper plate artificially corroded were used (Fig. 1a and 1b). Thickness of silver layer on silver plate is 5μm.

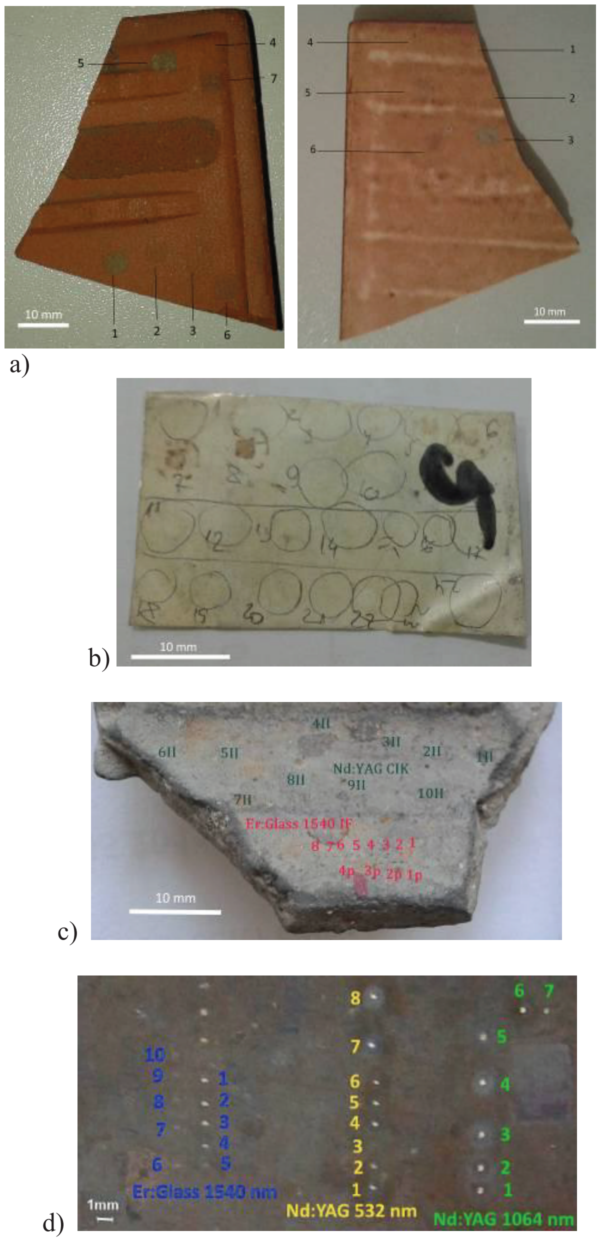


Fig. 1. Examined samples: a) ceramic tile glazed and unglazed sides, b) silvered copper plate, c) ceramic artefacts from region of Tyre and Sidon and d) brass plate

Additional investigations were conducted with laser irradiation of ceramic medival artefacts originated from archaeological sites from region of Tyre and Sidon, Lebanon and naturaly tarnished brass plate (Fig. 1c and 1d).

In the experiments, were used these lasers:

-Commercial Nd:YAG laser: Thunder Art Laser, produced by Quanta System: wavelengths 1064 or 532 nm; optical pulse duration <8 ns; output pulse energy up to 1000 mJ (λ=1064 nm) and 550 mJ (λ=532 nm). Repetition rate is 20 Hz, with a beam diameter of 10mm.

-Non-commercial nanosecond Er, Yb, Cr—Glass and Nd:YAG lasers developed in Institute of Physics, Center for photonics, Belgrade. Nanosecond Er, Yb, Cr—Glass laser emitting in the near-infrared (λ=1540 nm) which operated in the transverse TEM_{01} mode. Laser pulse duration (FWHM) was ~50 ns and pulse repetition rate 0.5 Hz. The energy of laser beam can be changed till maximal value of E=8 mJ. The pulse-to-pulse energy stability was $\leqslant$5%.

-Nd:YAG laser can operate with two wavelengths: ~~of~~ λ=1064 nm and λ=532 nm, TEM_{00} mode. Maximal values of laser beam energy for λ=1064 nm is 10 mJ, and for λ=532 nm is 10,2 mJ. In both case laser pulse duration is 80ns.

Optical microscope (OM) Olympus CX41, scanning electron microscopes (SEM) JEOL JSM-6610LB and JEOL JSM-639LV with energy-dispersive x-ray spectroscopy (EDX) INSA350, LIBS and XRF were used for the morfological and chemical analysis of laser radiation impact on the examined materials. XRF spectrometer, ARL TM PERFORM'X Sequential X-Ray Fluorescence Spectrometer (Thermo Fisher Scientific, Switzerland) equipped with a 4.2 kW Rh X-ray tube, which was able to determine all elements from Be to Am that are covered with our set of crystals: AX03, AX09, AX16C, PET, Ge111, LiF200 and LiF220. For qualitative analysis, spectral recording and data treatment, a software program Thermo Scientific TM OXSAS was used [7].

LIBS spectrometer is laboratory non-commercial system developed in Institute of Physics, Center for photonics, Belgrade [6]. This system is consisted of Er, Yb, Cr—Glass laser described before, optical system for focusing the laser beam and a spectrometer. Plasma emission was collected by the fiber spectrometer with the 600 mm core diameter fiber. The other end of the fiber is connected to CCD spectrometer (HR2000CG, Ocean Optics) which spectral range from 200 nm to 1100 nm, with a resolution of 1 nm.

TR200 Portable Surface Roughness Tester was used for prophylometric determination of the geometric parameters modification in irradiated zones and microhardness measuring for testing of micro-mechanical changes in the areas of laser irradiation with Micro Vickers Hardness Tester TH710.

B. Experimental conditions

The experimental parameters for some zones irradiated by Er:Glass and Nd:YAG lasers are presented in the table 1 for each of the samples.

All the irradiations were performed in the atmospheric conditions at the pressure of 1013 mbar, temperature of 293 K and standard relative humidity.

Within accessible lasers wavelengths, lasers parameters as are number of pulses (N) and energies of laser beams were changed in defining of optimal parameters for successfully and safely cleaning of brass surface without degrading the surrounding material.

Table 1 Experimental parameters

sample	laser	zone	E, mJ	λ, nm	N
ceramic tile glazed side	Nd:YAG	3I	130	532	200
	Nd:YAG	4I	130	1064	200
ceramic tile unglazed side	Nd:YAG	3II	130	1064	200
	Nd:YAG	2II	300	1064	200
ceramic artefacts	Nd:YAG	6II	120	532	200
	Nd:YAG	2II	300	1064	200
	Er:Glass	3II	8,1	1540	1
	Er:Glass	8II	2	1540	1
silvered copper plate	Nd:YAG	2	200	1064	200
	Nd:YAG	10	200	1064	1200
	Nd:YAG	17	200	532	1200
brass plate	Nd:YAG	1	10	1064	10
	Nd:YAG	4	10	1064	100
	Nd:YAG	1	10,2	532	10
	Nd:YAG	3	10,2	532	1
	Er:Glass	5	8,1	1540	1
	Er:Glass	10	2	1540	1

II. DESCRIPTION OF THE RESULTS

A. LIBS results

LIBS and EDX results of treated zones on all examined samples are analysed and compared. Comparison of LIBS spectrums of zone 5 of brass plate treated with Er:Glass laser (λ=1540 nm wavelength and laser beam energy 8,1 mJ) after 1 and 11 pulses are shown on figure 2. Picks were determined according [8]. There can be seen difference in Na, O, S, Fe peaks intensities between two plots which indicate that these elements are removed from surface, during laser cleaning.

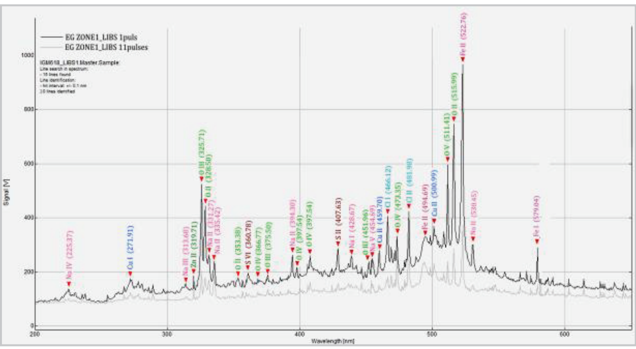


Fig. 2. LIBS spectrums of brass plate zone Er:Glass zone 5 treated with 1 and 11 pulses.

B. OM and SEM

OM and SEM results of silvered copper plate (fig. 3) show that, with applied laser parameters, no morphological changes in the zones irradiated with λ=1064nm wavelengths were found. Visually better cleaning is achieved with higher number of pulses. In the zone 17, which is irradiated with λ=532 nm wavelength, slightly removing of silver layer is found.

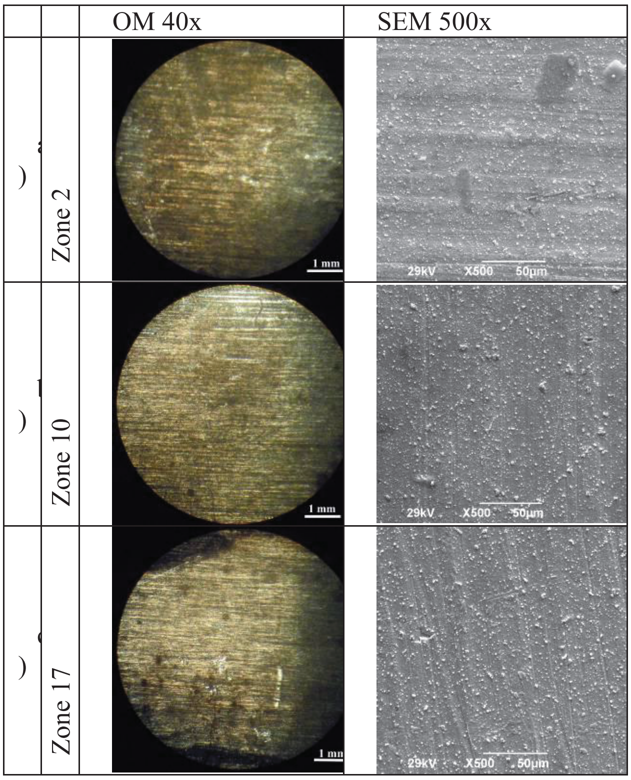


Fig. 3. OM and SEM analysis of silvered copper plate zones 2, 10 and 17

OM and SEM images of zones of brass plate treated by Er:Glass laser (figure 4 e) and f)) show that single laser pulse, with 2mJ, is sufficient to start cleaning of the corrosion layer. The higher energy 8,1mJ leads to the beginning of the base material melting.

Zones treated with Nd:YAG laser with λ=532 nm (figure 4a and 4b) and λ=1064 nm (figure 4c) and d)), all have melted base metal. All spots have the same dimmensions. The fluence and the number of accumulated pulses, applied in the presented tests, were up to the damage threshold. The extent of discoloration and melting depends on fluence level and applied number of pulses. The heat effect of the laser beam causes an oxidation process underneath the material surface, resulting in a color change on the metal surface.

A. EDX results

Silvered copper plate zone 2 EDX results (fig. 5) shows that irradiations with Nd:YAG laser, λ=1064 nm wavelength, 200 mJ laser beam energy and 200 pulses were not sufficient for satisfactory cleaning of sample surface. Beside Ag and Cu which are the base elements, there can be seen contaminant elements as are Ni, Zr, Cr, Fe, C, Si and O. When there are applied increased ammount of pulses, i.e. 1200 pulses (zone 10), there is observed significant changes in surface composition on cleaned zones. Only base material elements and C are present. In the zone 17 irradiated with same laser beam energy and number of pulses but with lower wavelength, satisfactory results of cleaning were achieved also, but there it can be seen slightly tarnishing, as a consequence of oxides presence.

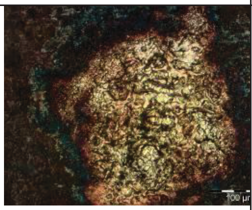
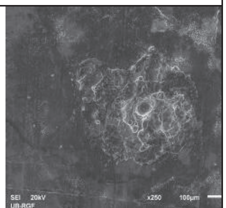
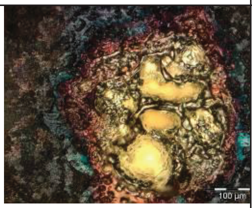
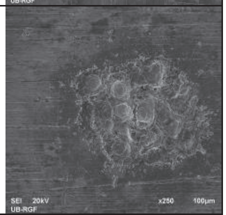
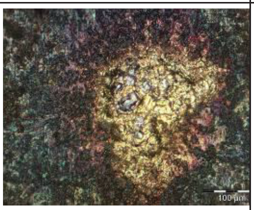
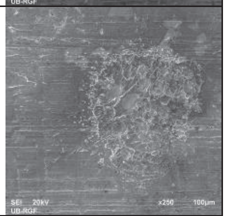
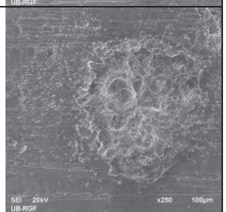
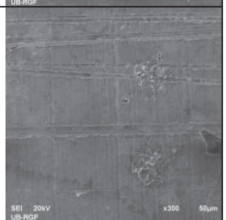
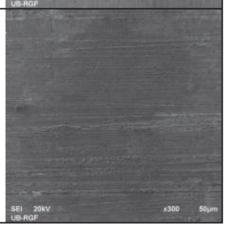
		OM 200x	SEM
)	Nd:YAG, Zone 1 (1064 nm)		
)	Nd:YAG, Zone 4 (1064 nm)		
)	Nd:YAG, Zone 1 (532 nm)		
)	Nd:YAG,Zone 3 (532 nm)		
)	Er:Glass, Zone 5 (1540 nm)		
)	Er:Glass, Zone 10 (1540 nm)		

Fig. 4. OM and SEM analysis of metal brass plate zones

EDX analysis of metal brass sample zone 10 (fig. 6) shows that elements P, S, Cl, and O are not visible on the Spectrum 1 recorded in the centre of zone, in contrast to spectrum 3 recorded out of laser cleaned zone. Layer of contaminant is removed. Slightly melting of surface is present.

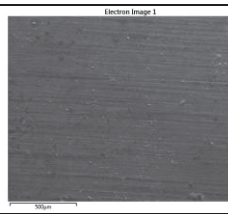
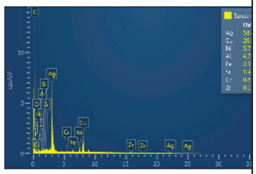
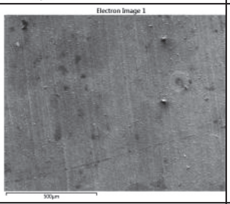
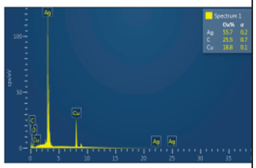
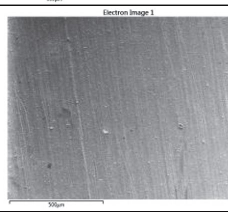
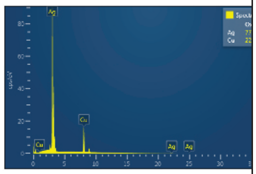
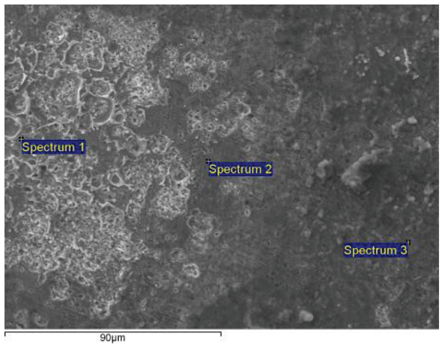
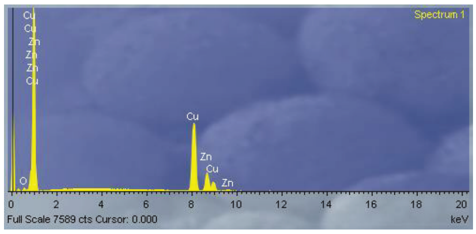
	one	SEM	EDX
)	zone 2		
)	zone 10		
)	zone 17		

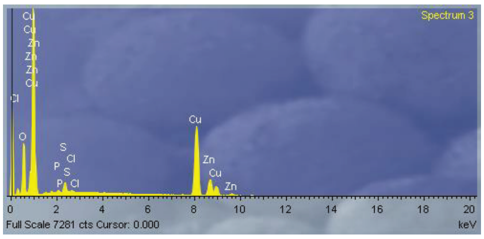
Fig. 5. SEM and EDX analysis of silvered copper plate zones 2, 10 and 17in a whole area



a)



b)



c)

Fig. 6. a) SEM and b), c) EDX analysis of metal brass plate zone 10

B. XRF results

The XRF analysis of contemporary ceramic sample confirmed that it is an aluminosilicate ceramic, consisted of SiO_2, Al_2O_3, Na_2O, MgO, K_2O, P_2O, TiO_2, and CaO xides (table 3)

Table 3 XRF analysis of glazed and unglazed sides of contemporary ceramic

oxides	Fe_2O_3	CuO	ZnO	ZrO_2	SnO_2	Sb_2O_3	BaO	HfO_2	PbO	SO_3
glazed	1.53	0.0129	2.21	23.18	1.20	0.164	0.112	0.387	18.66	
unglazed	7.12	0.0046	0.0384	0.0781			0.0659		0.0560	0.306
oxides	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	TiO_2	MnO	
glazed	0.837	0.594	6.37	39.27	0.0823	1.22	0.820	3.44	0.0238	
unglazed	1.20	1.36	21.96	62.50	0.273	3.14	0.614	1.80	0.0905	

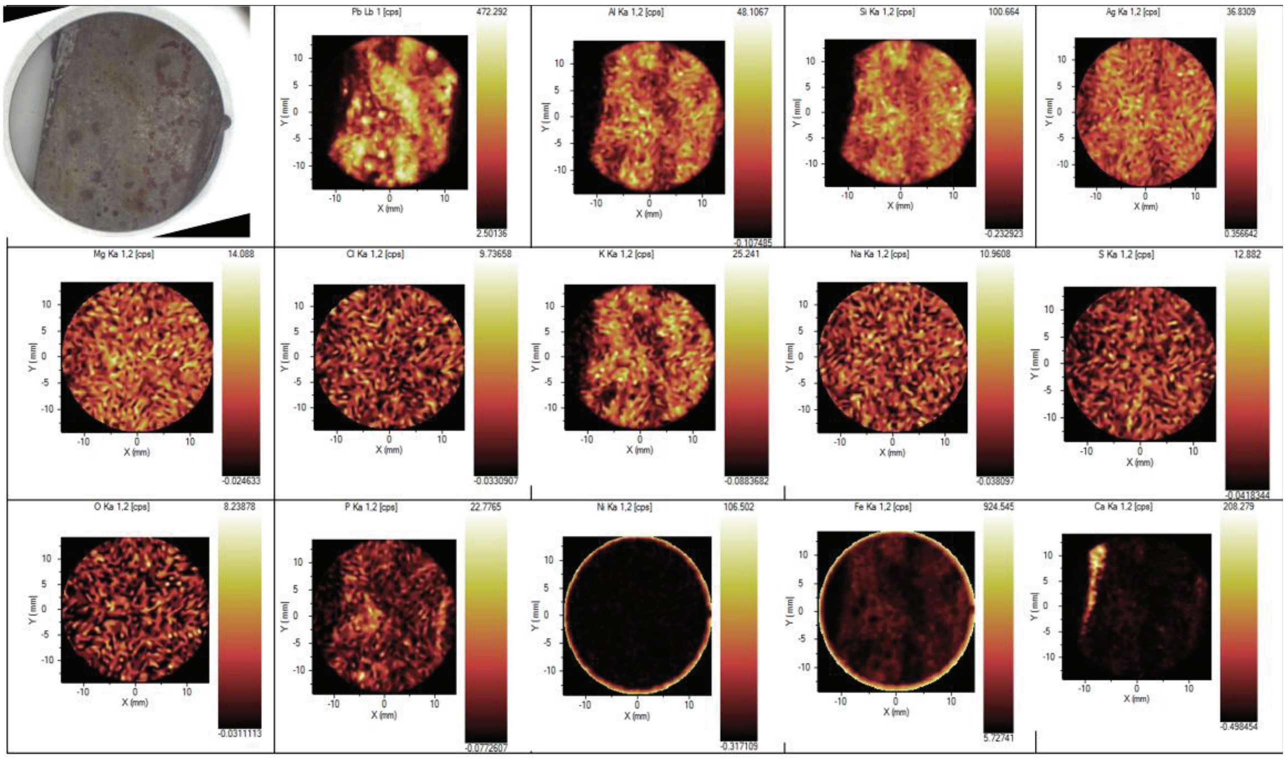


Fig. 6. XRF analysis of ceramic artefact

It can be seen significant presence of lead(II) oxide (PbO) which is used as a flux in ceramic glazes and zirconium oxide (ZrO_2) used to modify the visual appearance of the fired glaze.

Ceramic artefact XRF analysis (figure 6) identify aluminosilicate ceramic body with presence of MgO, K_2O, P_2O and Ag_2O uniformly distributed. Also the fragments of glaze are visible. On this areas the presence of PbO is above all other oxides.

C. Profilometry and microhardness

The roughness can be characterized by several parameters and functions (such as height parameters, wavelength parameters and spacing and hybrid parameters). The Mean Roughness (Roughness Average Ra) is the arithmetic average of the absolute values of the roughness profile ordinates.

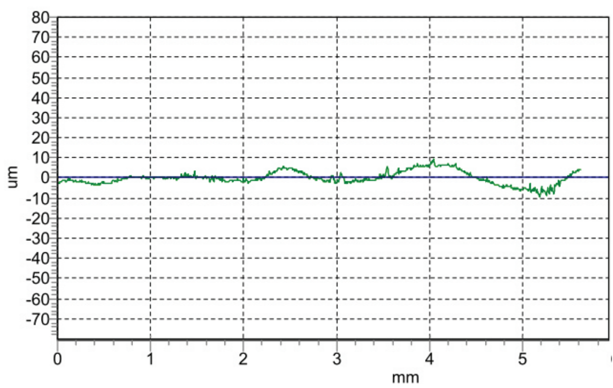


Fig.7. Profilometry above brass sample zones irradiated with Nd:YAG (1064 nm)laser

The results of profilometry test above brass sample zones irradiated by Nd:YAG (1064 nm) laser are presented in figure 7. Ra value measured on the zones array irradiated with Nd:YAG (1064 nm) laser is 2,491 µm. The depth of cleaned zones varies between 2.4 and 10 µm. Very similar results were recorded for Nd:YAG (532 nm) laser treated zones.

The variations of depths for Er:Glass laser cleaned zones are higher than for Nd:YAG laser.

Microhardness testing of irradiated material surface provides valuable information for the important material properties: resistance to deformation, friction and abrasion. Controlling these properties can contribute to a successful application of materials by helping to prevent wear and premature product failure.

III. CONCLUSION

The micro chemical and micro morfologycal properties of ceramic and metal surfaces treated with nanosecunds lasers, before and after the cleaning process, were examined using diferent analytical methods

The use of LIBS and XRF analysis shows successfully determination of differences in chemical composition of samples surface before and after process of laser iradiation and indicates the cleaning threshold parameters. Tests have shown that there is no significant difference in the composition of modern and archaeological ceramics. Damage thresholds are also very close, and morphological changes very similar, too.

Acknowledgments

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