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SURFACE MODIFICATION ON IRON INDUCED BY Nd:YAG PULSED LASER TREATMENT

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Abstract: *The modern military industry demands the most innovative and high-quality metals and alloys, as well as processing technologies. Iron and its alloys are a common material used for different types of weapons and military equipment. Lasers have been widely used in the metal surface processing, but the changes that occur on laser treated metal surfaces have not yet been sufficiently investigated. A study of morphological and chemical changes on the metal surface induced by Nd:YAG laser treatment in ambient air is presented. A pulsed Nd:YAG laser (1064 nm, Gaussian spatial profile, FWHM 8 ns, energy up to 525 mJ, beam diameter of 1-10 mm and fluence up to 3.5 J/cm^2) was used. Micro-morphological analyses of sample surfaces before and after laser treatment process were performed by optical and SEM microscopies. EDX method was used for chemical analyses and Spectra colorimeter for investigation of induced color changes. The laser irradiation effects were studied as a function of two laser parameters, number of laser pulses and laser fluencies, around and over the damage threshold. The results show that there are significant differences depending on these laser parameters.*

Keywords: *Nd:YAG laser, iron, surface treatement, SEM and EDX, colorimetry*

1. INTRODUCTION

Laser surface cleaning show many advantages compared to conventional chemical and mechanical cleaning methodes. It is fast, safe, and efficient. Being selective and contactless it can remove unwanted layer without damaging of base substrate. Also there is no wastes during and after process [1, 2].

For military purpose, laser cleaning is commonly used in corrosion control, non-destructive investigation, weld preparation, hazardous paint removal, small paint area removal and nuclear decontamination. This method is applicable for most materials: metals, ceramic, glass, wood, paper, marble, etc.

Application of adequate laser parameter and adequate working condition, for specific material, are a crucial for sucessful cleaning process. The most important cleaning parameter is the energy per unit area i.e. energy density (fluence) of the laser beam. In the case when threshold fluence is exceeded, damages or some modifications of the surface properties (hardness, corrosion or wear resistance, adhesion, etc.) may be expected. The other important parameters are laser beam wavelength, puls length, irradiation time. Hence, for satisfactory results, it is necessary to optimize adequate laser type and its parameters for specific material.

Of great importance for laser cleaning and laser metal processing is the examination of the interaction the basic material, in this experiment, iron, with the laser beam.

Investigation of cast iron cylinder bores treated with Yb-fiber lasers were made by Májlinger et al [3]. They found nanohardness of treated surface increasing and microhardness decreasing in comparation with base material. They explained it by the existence of an annealed volume beneath the top molten layer of the surface. TEA CO2 and Nd:YAG-lasers have been used to remove old adhesives and coatings from iron artifacts [4-6]. Removing of organic coating such as wax from iron objects using TEA CO2 laser can be carried out safely.

Ogbekene et al investigated laser cleaning of corroded grey cast iron brake disc with continuous wave CO_2 laser [7]. They found that the laser cleaning process increase the microhardness value in comparation with surface covered with rust.

P. Pasquet et al found that Nd:YAG laser cleaning was more efficient upon application of electrochemical potential on oxidised iron surface [8]. Radojković et al [9] examine the corrosion resistance of the Nd:YAG laser treated surface of iron artefacts.

Laser irradiation involves complex mechanisms such as photothermal, photochemical and mechanical effects on the material surface and the physical phenomena involved in laser cleaning or processing applications are not fully understood [10-13].

Surface color measurement is important for a very wide range of industrial applications including iron and steel marking and outher surface processing.

The aim of this paper was to investigate different changes generated on iron sample surface by Nd: YAG laser with λ = 1064nm.

2. EXPERIMENT

In the presented experiments, iron cube sample (dimension 1.9 x 1.6 x 1.2 cm) showed in Figure 1, was treated with Nd:YAG laser, Thunder Art Laser, Quanta System (with wavelength λ = 1064 nm, optical pulse length < 8 ns). The laser repetition rate is up to 20 Hz, with a beam 70 % fit to Gaussian energy distribution. During the experiment energy of laser beam, laser beam repetition rate and irradiation time were changed. Used irradiation parameters exceeded threshold fluence with aim to get insight in changes that occure on the surface above threshold. The sample surface was not mechanically cleaned before laser treatment, because it was not used for any purpose and there were not any visible contamination on the surface.

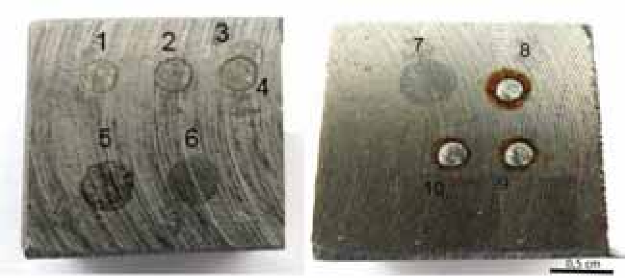

Figure 1. Iron sample with laser treated zones.

The laser parameters used for surface irradiation are presented in Table 1: λ = 1064 nm, the two energy values E = 425 mJ (fluence 2.8 J/cm^2) and E = 525 mJ (fluence 3.5 J/cm^2) and the laser spot diameter was about d = 4,5 mm. The specimen was placed in front of the laser head so that the laser beam was directed perpendicularly to the specimen. The experiment was performed in atmospheric conditions.

For morphological analysis after laser treatments on iron surface, USB optical microscope (OM) and scanning electron microscope (SEM) JEOL JSM-6610LV were used. Chemical analysis of irradiated zones were done by energy dispersive X-ray analysis (EDS). The same SEM/EDS device was used for the analysis of the chemical composition of the specimen surface.

Table 1. Experimental laser parameters on treated zones

Zone	E, mJ	*f*, Hz	t, s
1	425	20	10
2	425	20	30
5	525	20	10
6	525	20	30
8	525	20	60
10	525	10	60

SpectraWiz spectrometer OS V5.33 was used for color changes investigation on irradiated zones. The used colorimeter shows the results in the CIE L * a * b * (or CIELAB) space.

The instrument can provide wavelength information used to calculate sample absorbance, transmittance, reflectance and emittance [14-18].

3. RESULTS AND DISCUSSION

SEM and OM analysis

The laser irradiation results were observed and analysed by optical microscopy (Figure 2) and SEM microscopy (Figure 3). In all experimental cases there are visible changes on irradiated surface as conspicuous spherical zones. Applied laser beam energies were above threshold for safe surface cleaning and it caused surface material melting and concentric forms are visible after resolidification. In the case when lower energy was applied (zones 1 and 2, Figure 2), the surface darkening is present which is more intensive in zone 2 irradiated with longer irradiation time. This darkening can be explained by the thermo-chemical decomposition of $Fe(OH)_2$ and forming of FeO. Due to the laser beam interaction with oxide layer sufficient thermal effects induce additional thermal oxidation. The concentric rings inside zone are result of laser mode distribution. There is no laser effect in zone's surrounding. From the SEM images of these zones (Figure 3) can be seen laser-induced periodic surface structures (LIPSSs). Ripple formation can result from interaction between the laser-generated plasma and the melted iron [10].

In zones 5 and 6 (Figure 2) irradiated by the same experimental parameters as zones 1 and 2 but with higher laser beam energy, formed changes have the same shapes but greater intensity and blue colour. This indicates that the composition of the surface probably changes. The other explanation for colour change can be different refraction of light caused by deep complex forms and appeared after irradiation [11]. Also the different colours can be result of difference in the thicknesses of the oxidized layers. The thicknesses of these layers depend on operating laser parameters [11].

Around the zones irradiated with same laser energy but with longer irradiation time (Zones 8 and 10, Figure 2), the concentric yellow-brown rings are visible. Even lower repetition rate in zone 10, cause this change, but in a lower grade. SEM/EDS analysis (Figure 4) of these rings show presence of dark rings on the peripheral zones parts indicating that applied laser beam energy probably generate hematite and/or magnetite formation [13].

Morphological changes are observable in all irradiated zones, but mostly in the zones 2 and 10. When laser beam interacted with sample surface, a small amount of the surface was melted and evaporated, generating a high pressure vapour.

Interaction between laser iradiation and different surface layers depend on several factors, including laser processing parameters, laser beam wavelength, pulse width, thickness of oxide layers, and nature of oxide layers as well as substrate materials.

When the laser fluence is low, ablation photo thermal mechanisms include material evaporation and sublimation. With higher fluence, heterogeneous nucleation of vapour bubbles leads to normal boiling [12].

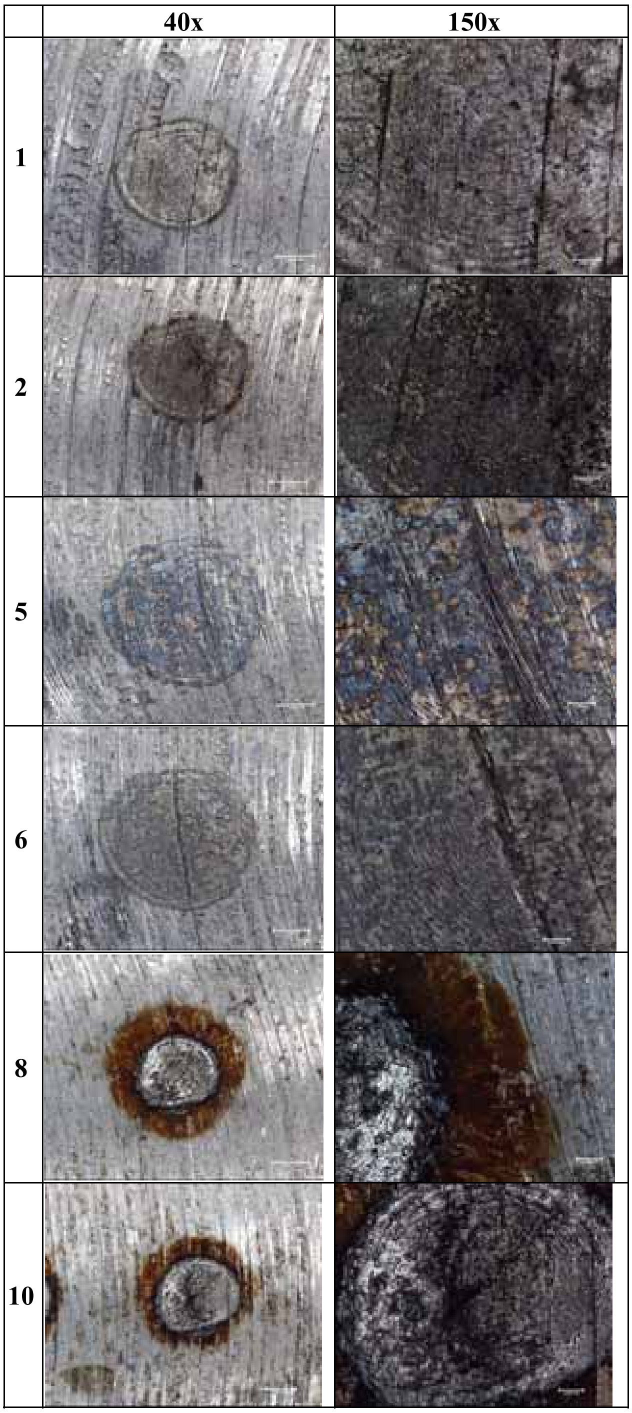

Figure 2. OM images of treated zones.

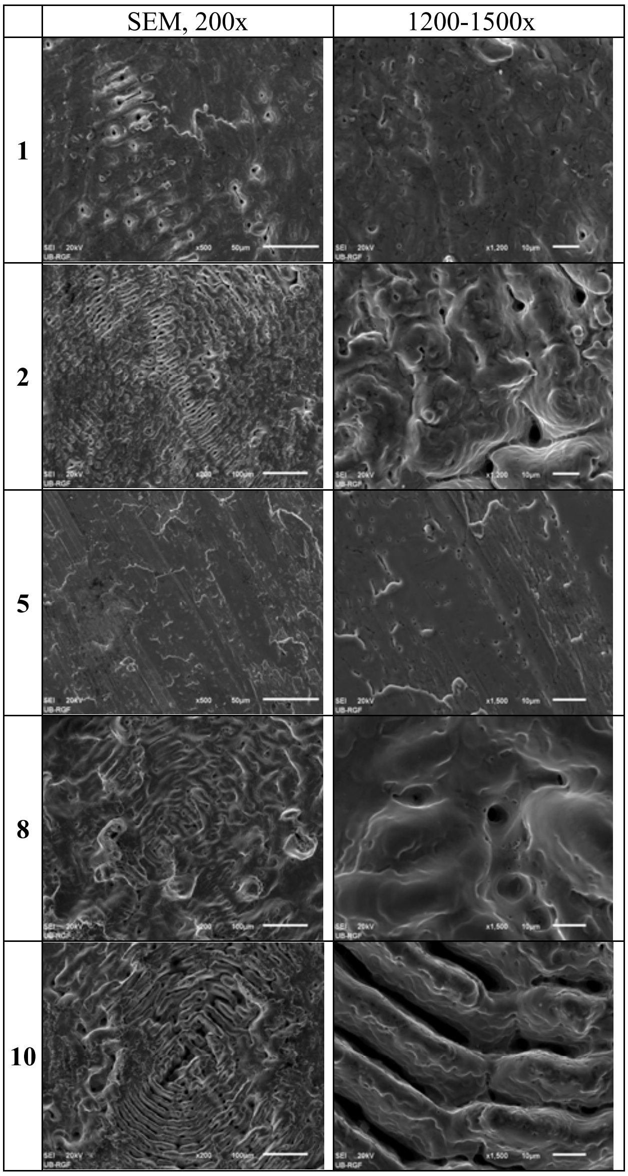

Figure 3. SEM images of treated zones.

EDS analysis

Qualitative and quantitative elements analysis on the irradiated zones and its surrounding were carried out by EDS method. Spectrums are recorded in zones 1 (Figure 4 and Table 2) and 8 (Figure 5 and Table 3). The composition of untreated iron surface is presented in Table 2 as well. From the results it can be seen that concentration of all elements was different depending on position of measurement point.

Spectrums 1 and 2 (Figure 4) present composition of the center of treated zone 1. There are visible sample surface melting, and presence of oxides. That indicate that applied laser parameters are not appropriate for safe and efective cleaning.

Spectrum 1 (Figure 5 and Table 3) is recorded inside the zone 8. Results show presence of O and C in the zone. Comparing with other spectra recorded in uncleaned surface around zone, concentration of these elements is lowest. Spectrum 5, which is recorded on the uncovered part around zone, also shows lower concentration of these elements.

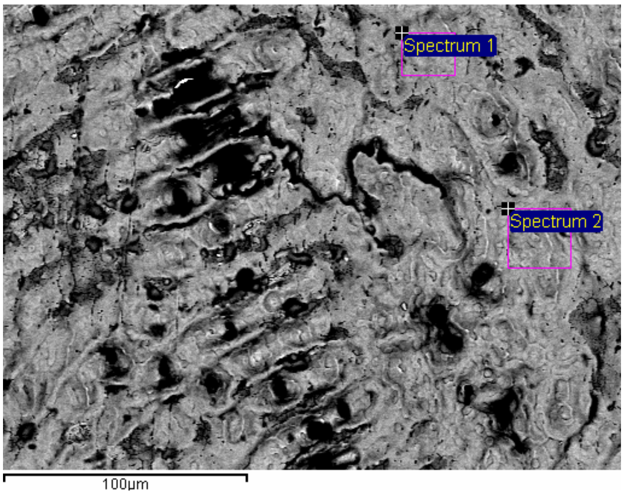

Figure 4. EDS analysis zone 1.

Table 2. Chemical composition of the zone 1 wt%

	C	Si	Mn	O	Fe
Spect 1	2.93	0.12	0.20	27.85	bal.
Spect 2	2.87	0.17	0.31	27.75	bal.
Untreated surface	2.27	0.53	0.57	0.00	bal.

Spectrums 2, 3 and 4 show composition of black deposits around the zone.

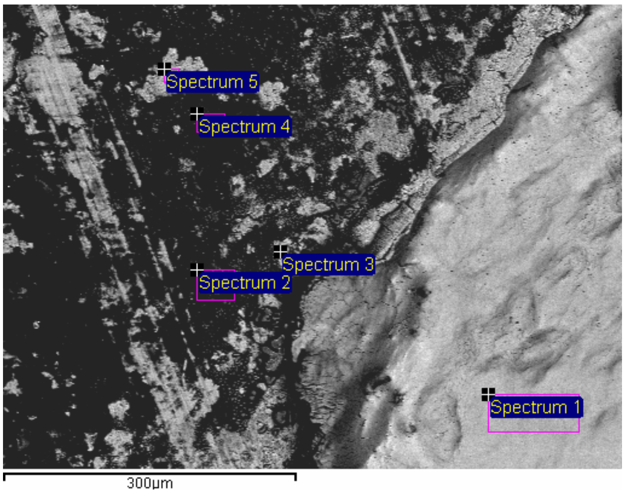

Figure 5. EDS analysis zone 8

Table 3. Chemical composition of the zone 8, wt%

	C	Si	Mn	O	Fe
Spec 1	1.32	0.16	0.27	28.91	bal.
Spec 2	12.95	0.18	0.43	46.41	bal.
Spec 3	7.40	0.12	0.45	36.14	bal.
Spec 4	16.78	0.12	0.23	53.41	bal.
Spec 5	5.65	0.21	0.43	32.95	bal.

Colorimetry of irradiated zones

The results of colorimetric tests for some zones are shown with diagrams in the CIELAB scale (Figure 6).

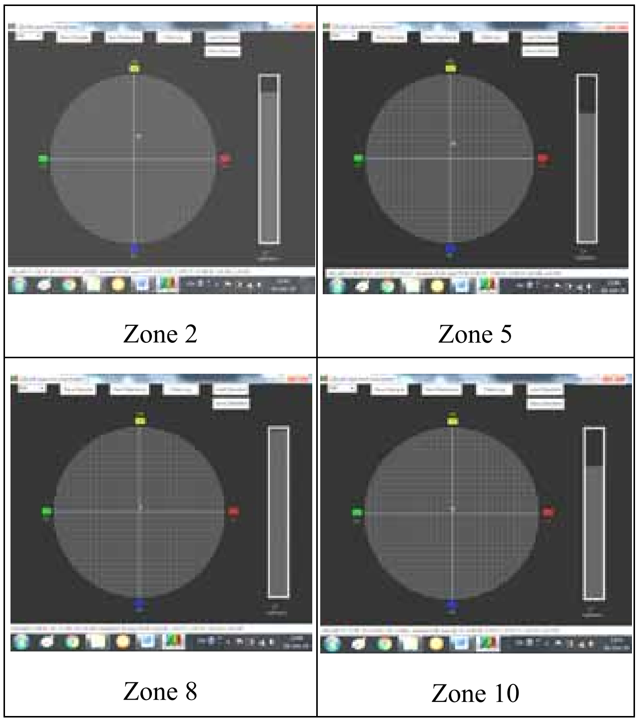

Figure 6. CIELAB diagrams for zones 2,5,8,and 10.

The sampling interval in a tristimulus integration affects the accuracy of a color coordinate performance. The CIELAB diagram shows the mean value of the information collected over the entire surface of the sample that is in the field of view of the instrument. Therefore, if the observed surface is not homogeneously colored, color variations that are on very small segments cannot be shown separately. The diagram shows the mean value of the tristimulus parameters. Figure 6 shows that in the zones of laser action there is a change in color from gray to gray-brown, as well as a change in the lightness from gray to white.

4. CONCLUSION

The main aim of this research was the investigation of the morphological and chemical changes on the surface of iron sample cleaned with Nd:YAG laser irradiation. The cleaning with higher laser beams energy lead to the melting of the metal and is not desirable for surface cleaning. Controled higher laser beams energy can be applied for different surface processing

The obtain results show that the laser interaction with materials is a complex process which depends on many parameters related to laser and sample. A proper and save application of lasers for cleaning or processing the iron surface, requires the comprehensive analyses of the material topographic and chemical modifications after laser treatments.

References

[1] Meja, P., Autric, M., Allloncle, P., Pasquet, P., Oltra, R., Boquillon, J.P., "Laser cleaning of oxidized iron samples: The influence of wavelength and environment", *Appl. Phys. A-Mater*. 69 (1999) S687–S690.

[2] Majumdar, J.D. and Manna, I., "Laser processing of materials", *Sadhana-Acad. P. Eng. S.* 28 (2003) 495–562.

[3] Májlinger, K. and Szabó, P. J., "Effect of leaser treatment on the surface of cast iron cylinder bores", *Mechanical Engineering* 54(2) (2010) 83–88.

[4] Koh, Y.S. and Sårady, I.: "Removal of adhesives and coatings from iron artifacts using pulsed TEA CO2- and Nd:YAG-lasers". Laser Techniques and Systems in Art Conservation/[ed] Renzo Salimbeni, Bellingham, wash.: SPIE - International Society for Optical Engineering (2001) 46-53.

[5] Koh, Y.S. and Sårady, I.: "Cleaning of corroded iron artefacts using pulsed TEA CO2- and Nd:YAG-lasers". *Journal of Cultural Heritage*, 4 (2003) 129-133.

[6] Koh Y.S., Sárady I. (2005) "Surface Cleaning of Iron Artefacts by Lasers. In: Dickmann K., Fotakis C., Asmus J.F. (eds) Lasers in the Conservation of Artworks. Springer Proceedings in Physics, vol 100. Springer, Berlin, Heidelberg

[7] Ogbekene, Y. F., Shukla, P., Zhang, Y., Shen, X., Prabhakaran, S., Kalainathan, S., Gulia, K. and Lawrence, J., "Laser Cleaning of Grey Cast Iron Automotive Brake Disc: Rust Removal and Improvement in Surface Integrity", *International Journal of Peening Science & Technology*, 1(2) (2018) 155 – 180.

[8] Pasquet, P., del Coso, R., Boneberg, J., Leiderer, P., Oltra, R., Boquillon, J. P., "Laser cleaning of oxide iron layer: Efficiency enhancement due to electrochemical induced absorptivity change", *Appl. Phys. A-Mater.* 69 (1999) S727–S730.

[9] Radojković, B., Jegdić, B., Bobić, B., Ristić, S., Polić, S., "Corrosion characteristics of laser-cleaned surfaces on iron artefact", *Zastita Materijala* 61 (1), (2020).

[10] Huang, Y., Liu, S., Zhu, H., "A Ripple Microstructure Formation on a Uniform melted Material Surface by Nanosecond Laser Pulses", *Physics Procedia* 22 (2011) 442 – 448.

[11] Amara, E.H., Haïd, F. and Noukaz, A., "Experimental investigations on fiber laser color marking of steels", *Applied Surface Science* 351 (2015) 1-12.

[12] Brown, M. and Craig, A., Fundamentals of Laser-Material Interaction and Application to Multiscale Surface Modification, chapter in Sugioka, K., Meunier, M., Piqué, A. (Eds.) Laser Precision Microfabrication, Springer-Verlag Berlin Heidelberg, 2010.

[13] Yandrisevits, M.A., Londero, P., Caro, F., Rizzo, A., Cappuccini, C., „Wavelength-dependent absorption and scattering effects on laser cleaning of a corroded iron alloy European scale armor“, Lasers in the Conservation of Artworks XI, Proceedings of LACONA XI, P. Targowski et al. (Eds.), NCU Press, Toruń 2017 (2017) 27-45.

[14] https://en.wikipedia.org/wiki/CIELAB_color_space (15.06.2020)

[15] Gräf S., et all, "Mechano-responsive colour change of laser-induced periodic surface structures", Applied Surface Science 471 (2019) 645–651

[16] https://www.xtlaser.com/laser-colors-on-stainless-steel-material-through-laser-technology/ (9/30/2019)

[17] Dusser B., " Controlled nanostructrures formation by ultra fast laser pulses for color marking", OPTICS EXPRESS 18 (3) (2010)2914

[18] Arkadiusz J. A., et al., "Laser-induced colour marking—Sensitivity scaling for a stainless steel", Applied Surface Science 264 (2013) 229–236.