INFLUENCE OF LASER MARKING ON STAINLESS STEEL SURFACE AND CORROSION RESISTANCE

Martin KUČERA, Michal ŠVANTNER, Eva SMAZALOVÁ

University of West Bohemia, Pilsen, Czech Republic, EU
kucera82@ntc.zcu.cz, msvantne@ntc.zcu.cz, smazal@ntc.zcu.cz

Abstract

Laser marking is the modern industrial application for non-contact surface modification. An incidence of a laser beam on the marked surface causes material and structural changes, which lead to optical changes of the surface. The processes during the laser-surface interaction can also affect other surface properties, especially corrosion properties in the case of stainless steel. Laser marking of stainless steel using the fibre pulsed laser SPI G3 is described in the contribution. Possibilities and limitations of steel laser marking are discussed. Some of the latest results of the material analysis and corrosion tests of the laser treated material are presented. Examples of laser marking influence on steel surface, structure and corrosion properties are shown.

Keywords: Laser marking, stainless steel, corrosion

1. INTRODUCTION

Laser marking is a material treatment method, which uses pulsed lasers and scanning heads. The laser marking is used for applications in the range from most common product marking to material surface structuring. Different processes can take place during the laser marking of a stainless steel surface - ablation, melting and heating. The surface is grooved, melted and oxidized. The optical configuration, the choice of the laser parameters and scanning parameters determine which processes occur during the laser marking [1]. The resulting configuration and parameter setting of the used laser marking device can affect the marked stainless steel surface structure and its elemental and phase composition [2]. The stainless steel surface influenced by the laser treatment has a different corrosion resistance compared to the base material. This behavior is very important for practical using of laser marking of stainless steels [3].

The interaction between the laser radiation and the metal surface is given by the material properties and by the properties of the laser beam. In the case of metals one part of the laser beam is absorbed while the rest is reflected. The absorptivity is the most important material parameter in the laser material interaction. The absorbed laser radiation causes different processes on metal surface. The interaction of single laser pulse with the metal can lead to heating, melting, vaporization, ionization, sublimation and direct dissociation. The decisive parameter is the peak power density P_p [W·cm^{-2}] which is given by energy of single pulse E_p [J], spot area A [cm^2] and the pulse length t_p [s]:

$$P_p = \frac{E_p}{A \cdot t_p} \tag{1}$$

It is possible to use several procedures from single lines to multi lines overlapping for laser marking of the surface of the stainless steel [3]. During heating and cooling of the steel surface the oxides on the surface grows. The thickness of the oxide layer is decisive for the darkness and color of the marked areas. The thickness of the oxide layer depends on the energy introduced in the surface - **heat input**. The heat input could be controlled by average laser power P [W], scan speed v [m·s^{-1}] and line spacing l_s [m]:

$$E_s = \frac{P}{v \cdot l_s} \quad (2)$$

If the parameters are suitable selected, the melting not occur and the oxide layer is created by reaction in laser irradiated area by the accelerated diffusion. High temperature gradients in the irradiated area accelerate the transfer of the particles and also cause initiating of the stresses, cracks and other defects. In case of thermal oxidation by pulsed laser, due to the short interaction times, the thermodynamic instable phases are created while other phases cannot be created.

The aim of experiments was to find out the used laser system marking parameters, which do not affect the corrosion properties of tested AISI 304 type stainless steel.

2. EXPERIMENTAL SETUP AND ANALYSES

The pulsed fiber laser SPI G3-HS with the ScanLab ScanCube 10 scanning head with f160 f-theta was used for laser marking. The maximum average output power of the laser is 20 W. The peak emission wavelength of this laser is 1062 nm and the maximum pulse energy is 0.8 mJ. The pulse repetition frequency could be set from 1 to 500 kHz and the pulse length could be 9-200 ns. The laser spot diameter in the focus distance is 70 um and the maximum scanning speed is 10 $m \cdot s^{-1}$. The SPI G3-HS lasers are usually used for marking (plastics, metals or poly-compounds), scribing, ablation, solar cell processing and other application [5].

Stainless steel sheets grade AISI 304 of the surface quality 2B was used for the experiments. The sheets were cold rolled and treated by a pickling and passivation operations. The microstructure of the steel is austenitic with marks of plastic deformation and it contains max. 0.07 % C, 17.5-19.5 % Cr, 8.0-10.5 % Ni, less than 1.0 % of Si, less than 2.0 % of Mn, less than 0.045 % of P and less than 0.015 % S. This type of steel is resistant against water, water vapor, atmospheric humidity or weak organic and inorganic acids. Sheets of 1.5 mm thickness were used. The dimensions of the samples for marking and corrosion tests were 150 x 100 mm and the dimensions of the samples for the XRD measurement was 20 x 20 mm.

2.1. Marking strategy

Strategy with multiline overlapping was used for the laser marking. This strategy creates oxide layer on the surface without melting the surface, when the process parameters are suitable. For this strategy is suitable use high scan speeds from 0.5 $m \cdot s^{-1}$ and the lines are very close to each other - from 10 to 100 micrometers. The marked area is scanned several times and the overlap of the lines is up to 95 %. The pulse repetition frequencies are over 100 kHz and therefore the time between the two pulses is less than 10 microsecond. The laser acts similarly as an area source due to fast scan speed and high repetition frequencies. The mark contrast depends on the heat input into the steel surface. The changes of the surface microstructure depend on the characteristic of the single pulses - pulse power density. The oxide layer growing depends on the combination of micro (pulse peak power density) and macro (heat input) characteristic of the marking process.

2.2. Corrosion test and analyses

The corrosion tests were performed according to ČSN EN ISO 9227 standards (exposure in a saline mist with 5% NaCl solution). 3D optical microscope Hirox KH-7700 was used for optical microscopy (OM) analyses. The scanning electron microscopy (SEM) analyses were realized by SEM Quanta200 from FEI with environmental (ESEM) mode. The structural and phase analyses of the samples after the laser marking were performed by XRD measurement. The whole surfaces of the samples of dimension 20 x 20 mm were laser marked and analyzed. The XRD analyses were performed for the samples without the corrosion exposition. Automatic powder diffractometer Panalytical X'Pert Pro with copper X-ray tube ($\lambda CuK\alpha$ = 0.154187 nm) was used for

XRD measurements. The Grazing Incidence X-ray Diffracton - GIXRD method, which is suitable for thin film measurement, was used for the XRD measurement. The constant incident-beam angle was 1° which corresponds to the depth of radiation penetration 1 μm.

3. RESULTS

3.1. Laser marking

Three different samples were marked. The first sample, **Fig.1**, with the fields of dimensions 15x16 mm was marked. The scan speed 800 mm/s and two different frequencies 200 and 400 kHz were used. The pulse length was 160 ns and the average power of the laser was 17.9 W. The fields on the sample I were marked with heat input in the range 0.2 to 3. J·mm^{-2}, step 0.2 J·mm^{-2}. The goal of the laser marking and corrosion test of the first sample was to find out the right process parameters window for the good corrosion resistance of marked fields.

Based on the corrosion tests results of the sample I, the samples II and III with expected good and reduced corrosion resistance were marked, **Fig. 2**. The fields 12x20 mm were marked by scanning speeds 400, 800 and 1600 mm/s, two different heat inputs and two pulse lengths, **Table 1**. The fields on the sample II for expected good corrosion resistance were marked by the heat input 1.4 J·mm^{-2} and pulse length 160 ns. The fields on the sample III for expected reduced corrosion resistance were marked with the heat input 3.0 J·mm^{-2} and pulse length 15 ns. All the samples were exposed in a corrosion chamber in saline mist for 120 hours.

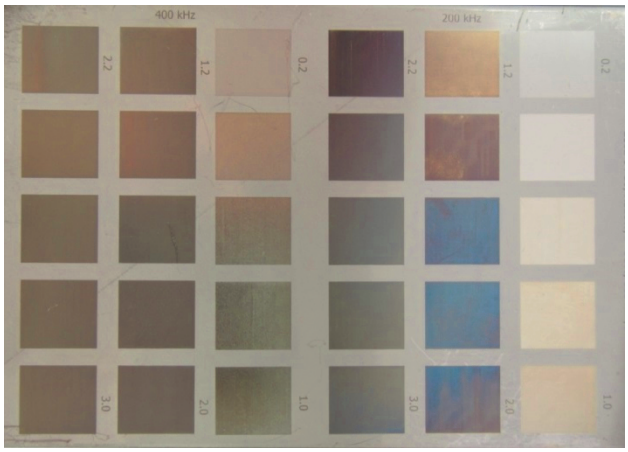

Fig. 1 The Sample I of the SS AISI 304, fields with heat input 0.2 - 3.0 J·mm^{-2}

Table 1 The comparison of peak power, peak power density, line overlap and heat inputs for marked fields on the samples II a III

Field no.	Frequency [kHz]	Heat input [J·mm^{-2}]	Pulse length [ns]	Peak Power [kW]	Peak power density [MW·cm^{-2}]	Line overlap [%]	Line spacing[μm]
1	200	1.4	160	0.54	14.0	78	15.4
2	200	1.4	160	0.54	14.0	89	7.7
3	400	1.4	160	0.27	7.0	78	15.4
4	400	1.4	160	0.27	7.0	89	7.7
5	150	3.0	30	2.32	60.3	88	8.7
6	150	3.0	30	2.32	60.3	94	4.4
7	250	3.0	30	2.23	59.6	80	14.3
8	250	3.0	30	2.23	59.6	90	7.2

3.2. Corrosion tests results

Different corrosion attacks of marked fields were observed on the sample I - from pitting corrosion to pitting with cracks. The sample I was after corrosion test analyzed by optical microscopy. The presence of corrosion attack was in range 0.02-0.23 %, the minimal corrosion attack (highest corrosion resistance) was observed for the heat input 1.4 J·mm^{-2}.

The marked fields with expected good corrosion resistance (**Fig. 2**, fields 1-4) were without corrosion attack. Some of marked fields only changed their contrast during their exposure in the corrosion chamber. The marked fields with expected poor corrosion resistance (**Fig. 2**, fields 5-8) were completely affected by surface corrosion. The corrosion tests and subsequent analysis confirmed the expected influence of laser marking parameters on the stainless steel samples corrosion resistance.

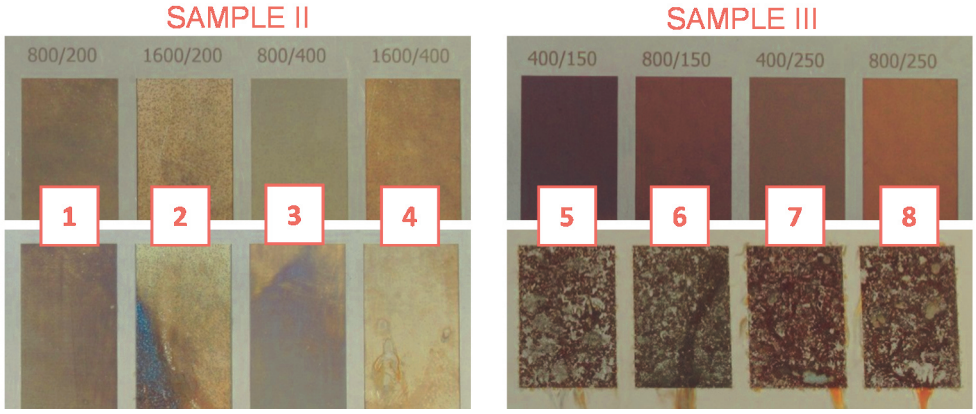

Fig. 2 The samples II and III of the SS AISI 304 before (top) and after (bottom) corrosion test

3.3. Optical microscopy and SEM

The cross sections of the marked fields on the sample I were evaluated by optical microscopy and scanning electron microscopy. The fields prepared with frequency 200 kHz and heat inputs 0.2 to 3.0 J·mm^{-2} were evaluated. The microstructure of the base material (AISI 304 stainless steel) is austenitic with plastic deformation marks caused by the rolling operation. The influence of the laser was observed for heat inputs 3.0 to 2.6 J·mm^{-2} using optical microscopy. It was possible to observe the influence of the laser also for heat input 2.2 J·mm^{-2} using the SEM.

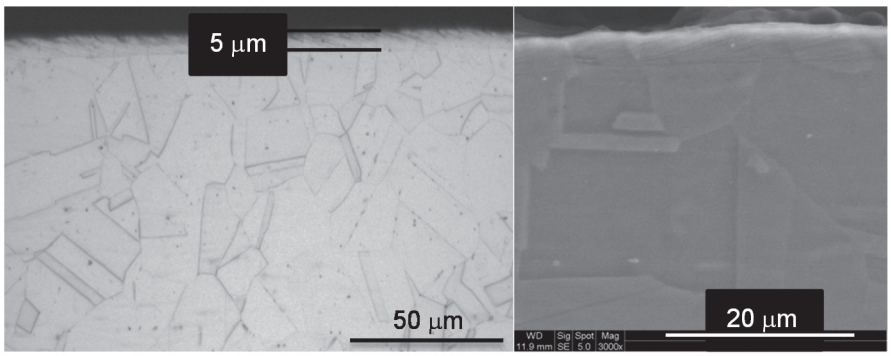

Fig. 3 The OM image (left) SEM image (right) of cross section of field marked with frequency 200 kHz and heat input 3.0 J·mm^{-2} after corrosion test

The laser marking did not affect the shape of the austenitic grains of the material. The depth of influence of the laser marking is 5 micrometers. The depth of influence of the laser marking is comparable for the fields marked with the heat input in range 2.2 - 3.0 J·mm^{-2}. For all of the evaluated fields was the pulse power density

14.5 MW·cm^{-2}. The change of heat input between the evaluated fields was realized by change of line spacing. This result shows that the depth of the influence is connected with the interaction of single pulse with the material surface.

3.4. XRD measurement

The XRD measurement was performed for base material and for the samples marked with identical laser marking parameters to the fields on the Samples I - III. The austenitic γ (cubic, face centered lattice) and ferritic α (cubic, body centered lattice) phases were identified in the base material. The oxide phase (cubic diamond lattice) was found in the laser marked fields in addition to the austenitic and ferric phase.

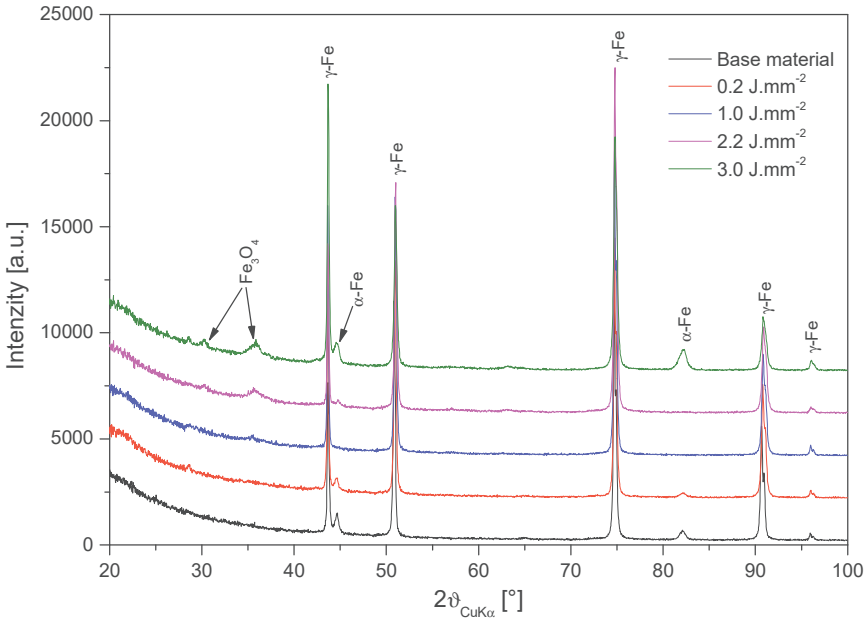

Fig. 4 XRD measurement of the fields (Sample I) marked width scan speed 800 mm/s, frequency 400 kHz, heat input 0.2, 1.0, 2.2 and 3.0 J·mm^{-2}, peak power density 7.3 MW·cm^{-2}

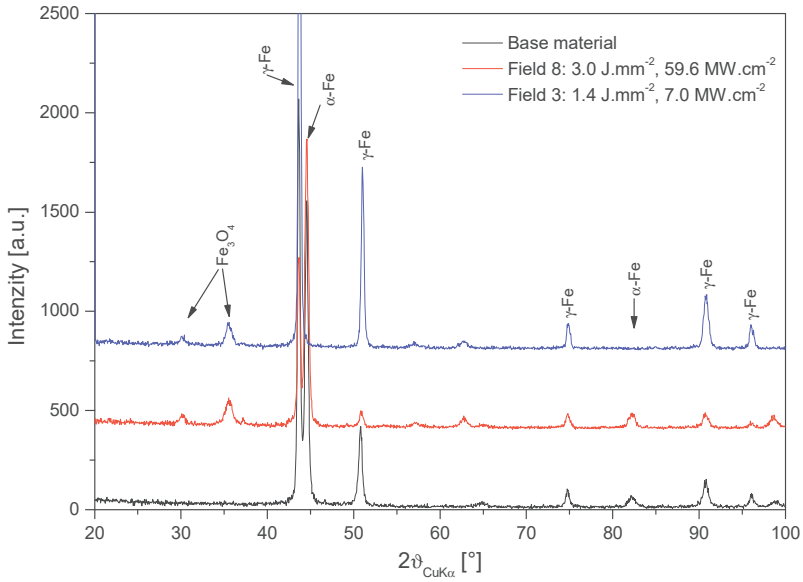

Fig. 5 XRD measurement of the fields 3 and 8 with good and poor corrosion resistance, marked with scan speed 800 mm/s, heat input 1.4 and 3.0 J·mm^{-2} with different frequencies and pulse lengths

The XRD measurement for the fields for frequencies 200 kHz on the Sample I showed the increasing of the intensity of the ferritic phase with increasing of the heat input. For frequencies 400 kHz showed the XRD measurement the decrease of the intensity the ferritic phase with increasing heat input up to heat input 2.2 $J \cdot mm^{-2}$, **Fig. 4**. The iron oxide Fe_3O_4 is detected for heat input above 1.0 $J \cdot mm^{-2}$ and the intensity of iron oxide phase increase with increasing heat input for both frequencies 200 and 400 kHz.
The XRD measurement was performed for the field 3 with the good corrosion resistance and for the field 8 with poor corrosion resistance, **Fig. 5**. The differences of the marking parameters between the fields 3 and 8 were the heat input and the peak power density, **Table 1**. The measurement showed the decreasing intensity of ferritic phase for area 3. The measurement for the field 8 with poor corrosion resistance showed the increasing intensity of ferritic phase compared to the base material. For both of the samples the iron oxide Fe_3O_4 was detected. The XRD measurement showed that the areas treated with the lower peak power density up to 15 $MW \cdot cm^{-2}$ contain less amount of the ferritic phase. The areas treated with the higher peak power densities over 50 $MW \cdot cm^{-2}$ contain higher amount of the ferritic phase.

CONCLUSIONS

We have shown that the laser marking of stainless steel significantly influences their surface and corrosion properties. The unchanged corrosion resistance is one of the very important requirements for stainless steel laser marking. The experiments showed that the laser marking processing parameters variation can lead to very different results from the point of view of corrosion resistance of the marked surfaces. It was verified that the most important processing parameters was the heat input and the characteristic of single pulses - pulse power density.
The aim of experiments was to find out the laser marking parameters for used laser system which do not affect the corrosion properties of stainless steel. It is possible to achieve this requirement with SPI-G3 fiber laser with the ScanLab ScanCube 10 scanning head with f160 f-theta objective. However, it is necessary to choose suitable process parameters. XRD analysis is a method, which can be helpful to find out the optimal process parameters combination.

ACKNOWLEDGEMENTS

This paper was prepared in the framework of and with the aid of instruments in the project CENTEM no. CZ.1.05/2.1.00/03.0088 co-financed by ERDF in the operational programme Research and Development for Innovation of the Ministry of Education of the Czech Republic and project no. SGS 2013-028.

REFERENCES

[1] Chen H., Shannon G., Brodsky M. Permanent Marking on Stainless Steels for Corrosion Resistance trough Control of Oxide Growth, Proc. of Int. Congress on Application of Lasers & Electro-optics ICALEO 2010, LIA, USA, Paper M501, 2010.

[2] Hendow T., Guerreiro P., Schilling N., Rabe J. Pulse Shape Control of a Mopa Fiber Laser for Marking of Stainless Steel and other Materials, Proc. of Int. Congress on Application of Lasers & Electro-optics ICALEO 2010, LIA, USA, Paper M604, 2010.

[3] ŠVANTNER M., KUČERA M., HOUDKOVÁ Š. Possibilities of stainless steel laser marking, Proc. of 21th Int. Conference on Metallurgy and Materials METAL 2012, Brno, Czech Republic, 2012.

[4] Laakso P., Ruotsalainen S., Pantsar H., Penttilä H. Relation of Laser Parameters in Color Marking of Stainless Steel, in Proceedings of the 12th NOLAMP Conference in Laser Processing of Materials, ATV, SEMAPP, Copenhagen, 2009.

[5] Gabzdyl, J. Micro-machining with Nanosecond Pulsed Fiber Laser Beams, Proc. of Pacific International Conference; Applications of lasers and optics; PICALO 2010.