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Influence of laser marking on stainless steel surface and corrosion resistance

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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 pulsed fiber 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: fiber; 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 material on the surface is removed, 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

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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 one of decisive parameters is the peak power density Pp [Wcm-2] which is given by energy of single pulse Ep [J], spot area A [cm2] and the pulse length tp [s]:

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

For laser marking of the surface of the stainless steel is possible using several procedures from single lines to multi lines overlapping [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 mark. 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]:

$$E_s = \frac{P}{v \cdot l_s} \tag{2}$$

When are the parameters suitable selected, the melting not occur and the oxide layer is created by reaction in laser irradiated area by the accelerated diffusion. The 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.

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 maximum pulse energy is 0.8 mJ. The pulse repetition frequency could be tuned 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.s-1. The SPI G3-HS lasers are usually used for marking (plastics, metals, etc.), scribing, ablation, solar cell processing and other [5].

For the experiments was used stainless steel grade AISI 304 of the surface quality 2B. The sheets were cold rolled and were after a pickling and passivation treatment. The microstructure of the steel is austenitic with marks of plastic deformation and it contains max. 0.07 % of carbon, 17.5-19.5 % of chromium, 8.0-10.5 % of nickel, 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. Plates of 1,5 mm in 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

For the laser marking was used the strategy with multiline overlapping. 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.s-1 and the lines are very close to each other – 10 to 100 micrometers. The marked area is scanned several times and the overlap of the lines is up to 95 %. The pulse repetition frequency are from 100 kHz and therefore the time between the two pulses is less than 10 microsecond. The laser acts as 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 (exposure in a saline mist with 5% NaCl solution) standards. The optical microscopy was realized on 3D optical microscope Hirox KH-7700. The SEM analyses were realized by SEM Quanta200 from FEI with ESEM mode. For the XRD measurements the automatic powder diffractometer Panalytical X'Pert Pro with copper X-ray tube ($\lambda CuK\alpha$ = 0.154187 nm) was used. For the measurement, the Grazing Incidence X-ray Diffracton – GIXRD method, suitable for thin film measurement, was used. The constant incident-beam angle was 1° which corresponds to depth of radiation penetration 1 µm. The samples after laser marking were measured.

For the experiment were marked two sets of samples The first were the samples, Fig.1, with the marked areas of 15x16 mm were marked with the scan speed 800 mm/s and with two different frequencies 200 and 400 kHz. The pulse length was 160 ns and the average power of the laser was 17.9 W. The areas were marked with heat input in range 0.2 to 3. $J \cdot mm^{-2}$ with the step 0.2 $J \cdot mm^{-2}$ to find the right process parameters window.

On basis of the results the corrosion test we marked the samples with selected parameters with expected good and reduced corrosion resistance, Fig. 2. The areas 12x20 mm were mark with scan speeds 400, 800 and 1600 mm/s and two different heat input and two pulse length. The areas for expected good corrosion resistance were marked with heat input 1.4 $J \cdot mm^{-2}$ and pulse length 160 ns. The areas for expected reduction of the corrosion resistance were marked with heat input 3.0 $J \cdot mm^{-2}$ and pulse length 30 ns. All the samples were exposed to the corrosion test in saline mist for 120 hours.

3. Results

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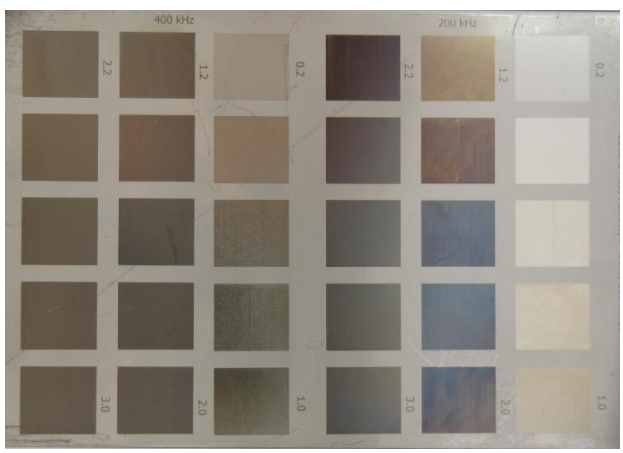

Fig. 1. The sample of the SS AISI 304, areas with heat input 0.2 - 3.0 J·mm^{-2}

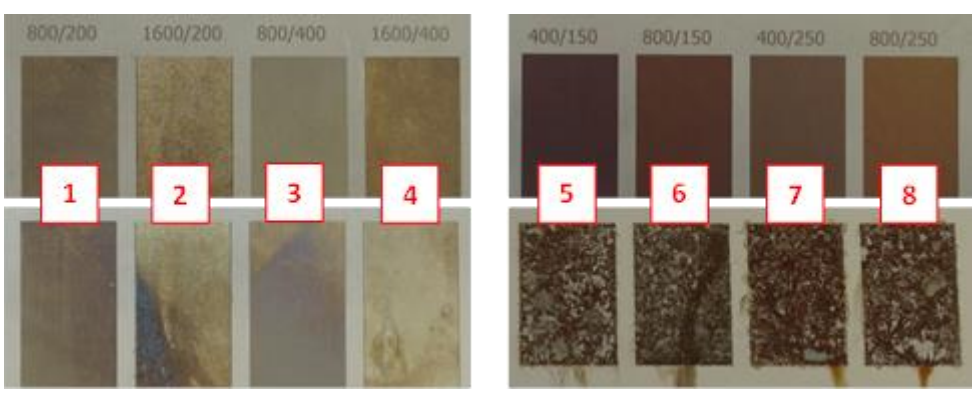

Fig. 2: The samples of the SS AISI 304 before (top) and after (bottom) corrosion test, areas with heat input 1.4 J·mm^{-2}, pulse length 160 ns (left) and 3.0 J·mm^{-2} pulse length 30ns (right).

1.1. Corrosion tests results

There were observed different corrosion attacks of marked fields from pitting corrosion to pitting with cracks. The sample, Fig. 1, with laser marked areas after corrosion test was evaluated by optical microscopy. The presence of corrosion attack was in range 0.02-0.23 %, the minimal corrosion attack was for heat input 1.4 J·mm^{-2}.

The marked areas with expected good corrosion resistance, Fig. 2 (1-4), were without corrosion attack. Some of marked areas only changed the contrast. The marked areas with expected poor corrosion resistance, Fig. 2 (5-8), were completely affected by surface corrosion. The corrosion test confirmed the expected influence of parameters of laser marking.

Table. 1: The comparison of peak power, peak power density, line overlap and heat inputs for marked areas.

Area 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

1.2. Optical microscopy and SEM

The cross sections of marked fields were evaluated by optical microscopy and scanning electron microscopy. The microstructure of the base material is austenitic with plastic deformation after mechanical treatment. The influence of the laser is possible to observe for heat inputs 3.0 to 2.6 J·mm^{-2}. For fields with lower heat input than 2.6 J·mm^{-2} is it not possible to observe the influence of the laser in cross section with optical microscopy. With the SEM is it possible to observe the influence of the laser also for heat input 2.2 J·mm^{-2}. The laser marking do not affects the shape of the austenitic grains of the material. The depth of influence is 5 micrometers and it is comparable for heat input in range 2.2 – 3.0 J·mm^{-2}. The depth of the influence is connected with the interaction of single pulse on the material surface. The pulse power density is 14.5 MW·cm^{-2} for all marked fields with the given frequency 200 kHz. The change of heat input is realized only by change of line spacing.

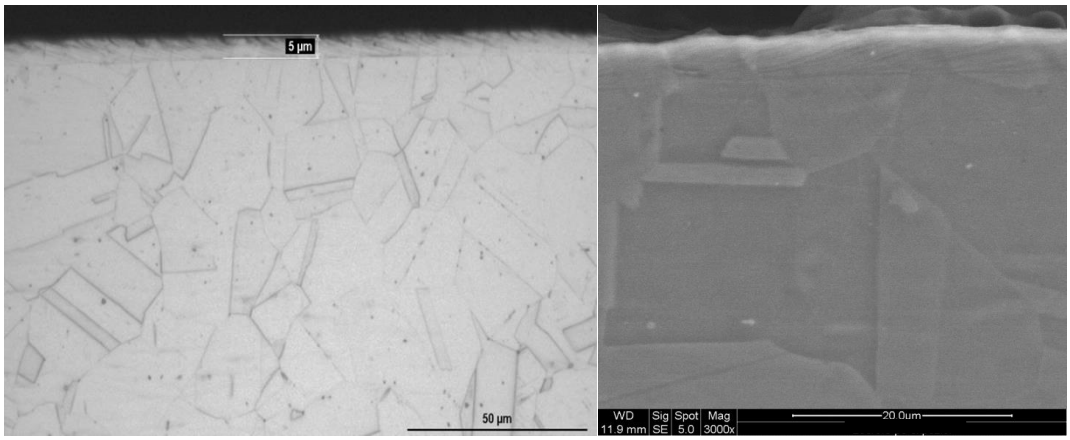

Fig. 3.: The OM image (left) SEM image (right) of cross section of field marked with frequency 200 kHz and heat input 3.0 J·mm^{-2} after corrosion test.

1.3. XRD measurement

The XRD measurement was performed for base material and both set of marked samples. The austenitic (cubic, face centered lattice) and ferritic (cubic, body centered lattice) phases were identified in the base material. The oxide phase (cubic diamond lattice) was found in the laser marked surfaces in addition to the austenitic and ferric phase.

For sample for selection of right process parameter window (Fig. 1), showed the XRD measurement for frequencies 200 kHz the increasing of the intensity the ferritic phase with increasing heat input. For frequencies 400 kHz showed the XRD measurement the decrease of the intensity the ferritic phase with increasing heat input to 2.2 J·mm^{-2}, Fig. 4. The iron oxide Fe_3O_4 is detected for heat input above 1.0 J·mm^{-2} and the intensity of corresponding iron oxide peaks increase with increasing heat input for both frequencies.

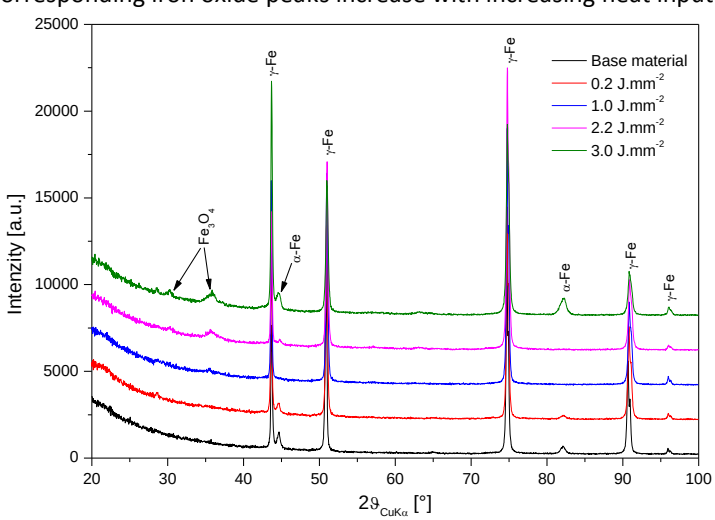

Fig. 4: XRD measurement of the areas of the samples marked width scan speed 800 mm/s and frequency 400 kHz with heat input 0.2, 1.0, 2.2 and 3.0 J·mm^{-2}.

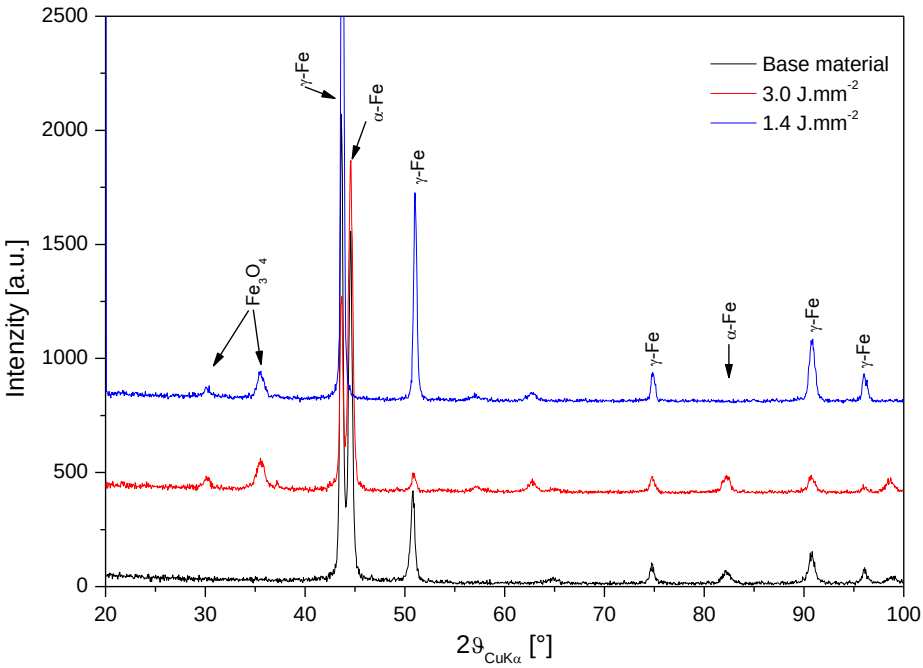

Fig. 5: XRD measurement of the areas 3 and 8 with good and poor corrosion resistance, marked with scan speed 800 mm/s, heat input 1.4 and 3.0 J·mm^{-2} with different frequencies and pulse length.

The XRD measurement was performed for the area 3 with the good corrosion resistance, heat input 1.4 J·mm^{-2}, and for the area 8 with poor corrosion resistance, heat input 3.0 J·mm^{-2}, Fig. 5. The main diference of the parameters 3 a 8 was except the heat input also the peak power density, Tab.1. The measurement showed the decreasing intensity of ferritic phase for area 3. It is consistent with the previous measurement for heat input 1.0 J·mm^{-2}, Fig. 4. The measurement for the area 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·cm^{-2} contains less amount of the ferritic phase. The areas treated with the higher peak power densities over 60 MW·cm^{-2} contains higher amount of ferritic phase.

2. 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 experiment showed that 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. This requirement is possible is possible to achieve with SPI-

G3 fiber laser with the ScanLab ScanCube 10 scanning head with f160 f-theta objective. It is necessary selection of suitable process parameters. XRD analysis is a method, which can be helpful to find out an optimum process parameters combination.

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