Marking decorative features to stainless steel with fiber laser

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Color marking on stainless steel has been available for sometime but still it has not been used widely in consumer products. Some industrial applications have been seen. New MOPA fiber lasers allow independent tuning of the pulse width and the marking process can be optimized for producing colors with better quality and visual appearance. Laser processing of metal surfaces creates an oxide layer on the surface. The thickness of this layer defines how white light is reflected from the sample. What in principle is only a thin oxide layer on the surface can be seen as different colors by the viewer. In this study, the visual appearance of laser marked surfaces was optimized by varying the pulse width, laser power, pulse energy and scanning velocity. The aim was to create uniform oxide layers on the surface, which would appear as high quality color marking. Marking quality was evaluated by visual examination as well as optical microscopy. Surface properties were measured using SEM-EDS and the effect of the viewing angle was examined using a spectral camera. The advantage of pulse width tuning is discussed based on these results. Application samples are presented.

Introduction

Color marking of metal surfaces is conventionally done by printing, anodization or emulsion coating. However, the scratch properties of printing are limited and anodizing more than a single color precisely is not easy. Emulsion coatings are more expensive and they require one step more to produce colors. Lasers can be used to create a permanent color mark on a metal surface as a one step process with a high throughput. Laser color marking of metals has been used for more than ten years with a variety of different laser sources /1,2,3,4/.

Despite the possibility to vary processing parameters typically in a wide range, some lasers are more suitable for color marking than others and the pulse width seems to be an important issue in defining the marking quality and contrast. Typical laser of choice for marking is a q-switched crystal laser which produces pulses in the nanosecond regime. These lasers do not allow independent adjustment of the processing parameters, but the pulse width is dependent on the repetition frequency and as the frequency changes, so does the pulse width. Therefore lasers that allow adjustment of the pulse width regardless of the frequency might give an advantage in marking.

In most applications laser marking is the fastest and the cheapest method. Flexibility of laser marking is based on writing with the laser beam, which interacts with the material surface creating the mark. Unlike most of the other marking techniques, laser marking does not use any chemicals or tools.

Some metals can be marked in a way that the surface appears colored. This is based on oxidation and the following thin film effect. In order to create an uniform and high quality mark, the used laser must have a good enough beam quality and stability. New fiber lasers are well suited for this method and their affordable price opens up new applications for laser marking. Color marking with lasers is easy and makes the surface visually more attractive. Suitable colors can be chosen by proper parameter control and if needed, the marking can be made on the fly on a moving object.

Principle of Laser Color marking

Surface oxidation of metals in an oxidizing agent is a well known phenomenon. Clean surfaces of many materials spontaneously react in air to form thin native oxide layers. Light-enhanced and in particular laser-enhanced material oxidation is based on thermal or non-thermal molecule surface excitations /5, p. 535/.

Thin oxide films can be formed by heating the surface uniformly using a laser beam. Oxygen must be present in the ambient atmosphere when marking with a laser. Air is sufficient for thin film growth, but a higher concentration of oxygen can be used to enhance film growth. Oxide film growth cannot be started in an inert atmosphere.
Most important parameters in laser marking are the focal spot diameter, power on sample, marking speed, line spacing, marking direction, repetition rate and pulse length. Gaussian beam profile of these fiber lasers might not be the best option for marking, but it would be modified into a top hat mode beam using a simple beam homogenizer.

The surface temperature and the thermal load, or the input energy over an area, can be adjusted by varying the beam power, scanning velocity or the line spacing. The aim is to maintain a constant surface temperature in order to create a uniform color surface. The following oxide layer will grow to a certain thickness and create the thin film effect. The process is self terminating because it comes less likely with increasing layer thickness /5, p. 536/.

The thickness of this layer defines how white light is reflected from the sample. What in principle is only a thin oxide layer on the surface can be seen as different colors by the viewer. If this oxide layer is thick and solid it will have also good corrosion and scratch properties, which are essential in consumer products. Variation in the oxide layer thickness and the surface roughness will have an effect to the resulting color seen by the viewer. Depending on the oxide layer quality, the color may change when viewed from different angles.

**Processing strategies**

Laser color marking can be done using different processing strategies. Figure 1 shows a surface which has been marked using a technique in which each line produces a certain thermal load to the material and the color is produced line by line. With this approach, the mark could also be single lines instead of an marked area. The laser power and the scanning velocity are adjusted in a way to create a proper oxide layer thickness in the illuminated region and the energy input can be expressed in units of J/mm. In order to create a surface which appears to have a uniform color, the line width has to be in the range of 20 to 50 µm. If the line is wider, the direction of the scan lines becomes visible. A narrow band of the base material can be seen between the colored lines, but these are not visible for the human eye. Overall, the surface in the Figure 1 appears blue.

![Figure 1. Micro figure of laser color marked SST.](image)

One other way to make an color reflecting oxide layer on the surface is to scan the area in a way that the marking lines overlap, Figure 2. The oxide layer is created by the accumulated energy of more than one line and the thickness of the oxide layer, i.e. the visible color, can be altered by varying the power, scanning velocity or the line spacing. The energy required to create a certain color is expressed in the units of J/mm$^2$. The down side to this approach is that last marked line often appears to be different in color, due to the change in the input energy in that area. However, if the line width is small, it is hard to recognize this without magnification.
In the two previous techniques, the surface has melted during laser processing and the oxide layer is formed during solidification and cooling. If the scanning velocity is high enough, it is possible to heat the surface uniformly and for a sufficiently long time to form the oxide layer without significant melting. In this approach the line spacing has to be small enough to bring enough energy to a surface area for oxide formation. As the scanning velocity is very high and the same area is scanned numerous times due to the small line spacing, the laser beam does not act as a point source of energy but more as an area source. The resulting oxide layer is very even and the marking lines cannot be seen even with a microscope, Figure 3.

Some lasers, such as the excimer laser, can deliver a beam which has a highly uniform intensity distribution and consequently a larger area can be heated evenly without moving the laser beam. Small color marks can be created with such lasers using a mask which defines the geometry of the illuminated area on the sample surface /6/.

All the previous methods can be made faster by doing the marking in an oxygen atmosphere. As the formed oxide layer is a reaction product of oxygen and a metallic element, a higher oxygen content, and therefore a larger quantity of oxygen available for the reaction, enhances the film growth rate and makes the marking process faster. The required
laser power for producing an oxide film of certain thickness can therefore be reduced. It is also possible that the faster oxide growth rate increases the absorptivity. Oxygen can also create an exothermic reaction which brings more energy into the process.

Researchers in Rochester University have made colors to metal surfaces with a fs-laser. In this case the color is not a result of an oxide layer, but nanostructures on surface of metal plate /7/. Overall, the process is very slow and economically infeasible due to the capital costs of such a laser.

**Experimental setup**

Two different fiber lasers were used in the experiments. The other one was a commercially available G3 20W pulsed fiber laser from SPI Lasers. The second pulsed fiber laser was developed by Fraunhofer USA, Inc. Center for Laser Technology (CLT) together with the University of Michigan /8,9,10/. The pulse width of the SPI laser could be tuned from 9ns to 200ns with 29 different variants. The Fraunhofer CLT laser allows continuous adjustment of the pulse width from a few nanoseconds up to 1 µs. The repetition range of the SPI laser is from CW to 500 kHz and the Fraunhofer CLT laser could be used between 10 and 100 kHz repetition frequency. Both fiber lasers are based on the Master Oscillator Power Amplifier (MOPA) approach. Together these two lasers offer a very wide range of parameters for laser marking.

SPI laser was connected to Scanlab Hurryscan II 14 with f160 f-theta and a 1-4x beam expander was used. Fraunhofer CLT fiber laser was connected to Scanlab SK1020 with 163 mm f-theta lens.

The common stainless steel grade AISI 304L was chosen for the experiments. Plates of 1 mm in thickness were used and the plates were laser cut to a size of 5 by 6 cm. Surfaces were cleaned with normal acetone before marking since even fingerprints could have a marked effect on the resulting color or the oxide layer thickness.

The results were evaluated based on visual examination as well as optical microscopy. SEM and SEM-EDS were used to get high magnification images of the formed oxide layer and also to detect the chemical composition of the surface.

**Results and discussion**

**Oxide film growth**

Investigation of the laser induced oxide layer was done with an SEM microscope. The marked samples were machined into a specific size before the SEM examination and the image of the oxide layer edge seen in Figure 4 is taken from an area close to the machined edge. The thickness of the oxide layer could only be measured from it’s cross section and machining the parts created a good edge for measurement. Visible color of the sample in Figure 4 is dark green. Laser parameters were 15 W, 85 kHz, 2000 mm/s, 1.2 µm line spacing. The spot size was 45 µm. The oxide layer thickness grown with these laser parameters was approximately 310 to 340 nm. As can be seen from the figure, the oxide film is rather uniform in thickness, therefore creating a even colored surface.
Figure 4. SEM-Figure of marked SST. Visible color green.

Figure 5 reveals the atom count of the surface and indicates that the film consists of chromium oxides. The curves on the left represent the marked surface and the curves on the right show the atom count from the base material. The measurements cannot be used for an accurate estimation of the oxide film composition. Since the oxide film is only some hundreds of nanometers in thickness, the measurement partially reaches the metal surface, altering the results. However, the variation in the Oxygen, Chromium and Iron content is evident. The main alloying elements and their mass fractions in the 304L grade stainless steel are 2 wt% Mn, 18 to 20 wt% Cr and 12 wt% Ni. As seen from Figure 5, the atom count of Iron is naturally the highest, the Chromium count is approximately 800 and the Oxygen count is in the range of 350 to 400. The steel itself contains only a limited amount of oxygen and the measured oxygen count is from the surface.

When the surface is treated with the laser, the amount of these elements changes. The mean Iron count decreases by more than half, the amount of Chromium decreases to approximately half of its original content and the Oxygen count doubles. Many of the other alloying elements should not be present in the oxide film and the counts shown come partially from the base material. Based on these measurements it is not possible to define the exact type of the oxide layer. The Oxygen, Iron and Chromium amounts and their fraction in the film composition can vary depending on the processing methods and parameters.
Effect of the processing parameters on the color formation

MOPA fiber lasers allow very free adjustment of the processing parameters and the parameter space is very large. In order to optimize the process one can adjust the pulse width, repetition rate, average power and scanning velocity. Further, the combinations of these parameters produce different pulse energies and peak powers. The peak power $P_{peak}$ during a square pulse can be calculated by

$$P_{peak} = \frac{P}{t_p \cdot f}$$  \[1\]

or

$$P_{peak} = \frac{E_p}{t_p},$$  \[2\]

in which $P$ is the average power [W], $t_p$ is the pulse width [s], $f$ is the pulse repetition rate [Hz] and $E_p$ is the pulse energy [J]. The pulse energy can be calculated by

$$E_p = \frac{P}{f}.$$  \[3\]

Due to the vast number of parameters, experiments were designed in a manner to keep several parameters constant while adjusting the others and thus establishing the effect of the processing parameters individually. Both of the lasers were used in the experiments. The parameter spaces of the lasers overlap in some respect, but in order to learn about the effects of the processing parameter in a wider sense, the SPI fiber laser was mainly used at repetition rates exceeding 100 kHz and the CLT fiber laser was used also with longer pulses, up to 1 µs.

Samples were marked by scanning lines side by side with an either 25 or 30 µm spacing and varying the scanning velocity to change the input energy per area. Each line was scanned from left to right, to avoid any thermal cumulation in the edge areas which bi-directional scanning would cause. Both lasers delivered a beam of an approximate diameter of 30 µm on the work piece surface using a 160 or 163 mm f-theta optic for focusing the collimated beam. The marking area for a single parameter combination was 2 by 2 mm. For each set of laser parameters (pulse width, power, frequency) a 5 by 10 sample parameter matrix was marked in which the scanning velocity changed from sample to another gradually with small steps from 20 to 212 mm/s. Altogether this resulted in 50 different scanning velocities, each creating a slightly different appearance of the surface. An example of 6 parameter matrixes on a stainless steel plate is presented in Figure 6. The purpose of the present study was not so much to optimize given colors, but to reveal the effect of the independent parameters on the marking quality.
Since the oxide layer thickness is the dominant factor in determining the visual color of the surface, in most cases the colors appear in a similar sequence. Slowest velocities create a dark surface, which does not reflect light in a certain color. In such a case the layer is sufficiently thick to absorb most of the visible spectrum. Highest scanning velocities produce a surface which appears glossy, but also does not appear colored. In this case, the laser pulses remelt a thin layer on the surface and the rapid resolidification and fast cooling produces a shiny surface, which does not have sufficient time to form an visible oxide layer. Between these two extremes colors brown, blue, green, red, purple and gold can be produced. The contrast and order of these colors may vary depending on the laser parameters.

**Results of basic marking tests**

First set of experiments was done using an average power of 4 W. The pulse width was varied between 30 and 180 ns, and the repetition rate was varied between 400 and 66.7 kHz. These two parameters were varied in a way to produce a constant peak power; short pulses were used with high repetition rates and vice versa. The peak power was constant at 333 W. Best colors were produced using a pulse width of 90 or 120 ns and a repetition rate of 133 or 100 kHz, respectively. These parameters resulted in a pulse energy of 30 and 40 µJ. Higher or lower repetition rate did not produce colors that would appear as good. Most of the squares marked using the high or low repetition rates appeared brown with shades of other colors. Results from these experiments can be seen in Figure 7.

In the second set of experiments the repetition rate was kept constant at 100 kHz and the similar 333 W peak power was used for all of the samples. The pulse width was varied from 90 to 180 ns and the average power from 3 to 6 W. The purpose was to find out whether the parameter area that resulted in good quality colors during the first experiments were the result of the correct repetition rate or the pulse width. It was found that the best colors were produced again at around 100 ns pulse width. It should however be noted that since the peak power was kept constant, using a longer pulse also meant using a higher average power and pulse energy. In these cases, use of higher scanning velocities might create some colors. But using the similar velocities as in the first set of experiments, the samples marked at 5 or 6 W
average power and a 50 or 60 µJ pulse energy, respectively, resulted in low quality and mostly brown or gold surface finish.

The first two sets were marked using a fixed peak power of 333 W and adjusting the other laser parameters. Judging by the results, most of the good colors were produced using a 30 or 40 µJ pulse energy. The next set of experiments was done using a constant 40 µJ pulse energy. In order to keep the pulse energy constant, the average power was set to 1, 3, 4, 6 or 8 W and the repetition rate was 25, 75, 100, 150 or 200 kHz, respectively. The pulse width was constant at 120 ns. In all of the cases, the colors are rather good with the exception of samples marked at 1 W average power and a repetition rate of 25 kHz. In this case the pulse energy is similar to the other experiments, but the low average power does not deliver enough energy to the area to create a thick enough oxide layer. The pulse energy is sufficient to melt a thin layer on the surface and the marked area appears polished. The color can be interpreted as silver. Test matrixes marked at 3, 4, 6 and 8 W power all produced a good spectrum of colors.

In order to more precisely determine the effect of the peak power, which at a given average power and repetition rate is determined by the pulse width or the pulse energy (see Eq 2), a set of experiments was made using a fixed average power of 4 W and the established optimal pulse energy of 40 µJ. The pulse width was varied between 30 and 180 ns, resulting in a peak power of 222 W to 1.33 kW. Interestingly the shortest pulses, 30 ns, resulted in the most variety of different colors. Areas marked with 60 ns pulses appeared mostly brown and areas marked using pulse widths of 90 to 180 ns all created similar colors, the only difference being the more glossy finish and a limited viewing angle compared to the markings at 30 ns pulses.

Marking at high repetition rates
A set of experiments was carried out using the full scale of repetition rates ranging from 50 kHz up to 500 kHz. The average power was kept constant at 4 W and thus the pulse energy varied between 80 and 8 µJ, respectively. Pulse width was 120 ns. Lowest repetition rates started to ablate material from the surface and resulted in poor marking quality. Higher repetition rates resulted in better colors, each of them having different tones. The highest repetition rate also formed some colors, but the quality of these was limited.

Marking at pulse width of 100 ns up to 1 µs
A wider range of pulse width values was also tested, ranging from 100 to 1000 ns. The repetition rate was set to 100 kHz and the average power was 4 W. Therefore the pulse energy was 40 µJ and the peak power was defined by the pulse width, ranging from 40 to 400 W.

1 µs pulses produced rather good, but light colors. In this case the physical phenomenon of the color formation is rather different from the shorter pulsed experiments. The appearance of the surface is very dependent on the viewing angle and is directional. Therefore the oxide layer is possibly not the only phenomenon responsible for reflecting colors from the surface. Further microscopic investigation of the treated surface shows that at correct processing velocities the pulse to pulse distance is approximately 1 µm. Each pulse creates a similar melt pool and when resolidified, the melt pool edges create a diffracting surface. Such a surface is presented in Figure 8. The surface does not have a red color in real life as the figure has, but the color is caused by the DIC optics used for taking the microscopic image.

Figure 8. A laser marked surface in which the pulse to pulse distance creates a grating which reflects different colors depending on the viewing angle.
Pulses of width 500 to 1000 ns all produced a similar surface appearance, and in all of these cases the surface color depends highly on the viewing direction and angle. The best results were achieved using a pulse width of 100 to 150 ns and a 30 to 40 µm line spacing. The slowest tested scanning velocities produced a dark green surface and gradually increasing the velocity the color changed from green to purple, red, blue and finally gold and silver.

Overall, the following conclusions can be drawn from the various marking experiments performed with the two MOPA fiber lasers in a very large parameter space. All of the results are related to the focal spot diameter, which was in both cases approximately 30 to 35 µm. Varying the focal spot size has a marked effect on the marking quality and for the power levels used in this study, the focal spot diameter of 30 to 35 µm produced the best results.

The energy used in the marking process can be divided into two different schemes; first one is the pulse energy, which determines the amount of energy brought to the surface during a single pulse \[ J \]. This energy is dependent only on the average power and repetition rate (see Eq 3). Laser pulse of a given energy can either heat, melt or evaporate the interaction area at the surface, depending on the peak power, which is determined by the pulse width. The second scheme is the energy input per area unit \[ Ws/mm^2=J/mm^2 \], which is defined by the marking time \[ s \] and the power \[ W \], the marking time naturally depending on the scanning velocity and the line spacing. Both of these schemes have an effect on the surface’s visual appearance after marking.

It was found that many different parameter combinations produced useful colored surfaces. In the power range used, most of the applicable colors were marked using a pulse energy of 10 to 40 µJ. Above these values, the thermal impact of a single pulse was too high and the surface becomes gray/brown. The next limiting factor was the pulse width, which determined the peak power. When comparing the best blue, red, green and gold colored surfaces produced with both of the lasers, all of them were produced using a 120 ns pulse width and a 100 to 350 kHz repetition rate. Using shorter pulses or lower repetition rates resulted in less clear colors. Also, when a very high frequency, >400 kHz, was used, the pulse energy was too low to create a desired impact to the surface. This leads to the assumption that if the peak power exceeds a value of approximately 500 W or is less than 100 W, the marking quality is compromised. The only exception to these findings is the parameter set marked using a 100 kHz repetition rate, 4 W average power and a short 30 ns pulse width. This parameter combination reached a high peak power value of 1.3 kW, yet the produced colors were clear. In this case it can be assumed that the process is a combination of evaporation and melting, creating an optimal thermal cycle for marking. If the process is based on evaporation, the micro roughness created during marking would explain the wider viewing angle.

After finding the optimum pulse parameters, most of the colors can be produced only by changing the scanning velocity, i.e. changing the energy per area unit, which determines the thermal load to the material and thus has the greatest effect on the oxide layer thickness and color.

**Effect of the viewing angle**

Since color marking is based on reflection of light from the metal surface through the thin oxide film, the viewing angle is obviously an important issue. The marking direction and design of the image, logo or pattern can be contrived in a way that the product is normally being viewed from the angle to which light reflects in the most attractive manner. If the marking is done to a product which is stationary, the ambient lighting can be designed so that the color marked surface catches the eye of the viewer.

Laser parameters can also be selected so that a proper visual appearance is created depending on the product, it’s use and location. When the parameter range is such to smoothly melt the material surface, the geometry of the surface becomes smooth, and the optimal viewing angle has to be more precise. If the laser beam can actually produce a surface which is uneven, but the oxide layer is uniform, it is possible to see the color from a wider range of viewing angles, as the light is scattered in stead of reflecting into a single direction from a planar surface. Confirming these assumptions and optimizing the process while keeping the viewing angle in mind still requires more experimenting.

Figure 9 shows the measurement of color marked sample under standardized lightning conditions. Laser processing parameters were 4 W laser power, 100 ns pulse width, 48mm/s scanning velocity, 40 µm line spacing and 100 kHz repetition rate. Results show how the viewing angle has an remarkable effect on how the sample is seen by the viewer. Surface roughness would increase this brightness of color value. Due to test conditions lightning could not be adjusted over 75°.
Decorative features on consumer products and outlook to the future potential

Laser engraved products have been on the market for consumers for a long time but laser color marked products are to be seen later. One good example could be personalization of electronic gadgets. There has been laser engraving applications available for some time but since SST has been more commonly used nowadays in these gadgets the color marking would also be available. Figure 10 shows a laser color marked front panel on telecom product. Red color gives a nice touch to the otherwise simplified outlook.

On forks and knives the stainless steel texts have been used for ages with black outlook. Now manufacturers would have possibility to add decorative features on normal forks and knives with color marking.

Company logos on products would also be potential application to color marking (Figure 11.).
In the coming years laser color marking is sure to take a bigger role in marking due to the high demand for consumer product customization. There are a lot of applications in which laser engraving is used and when color marking is a mature enough process, it will replace many of those applications. On the other hand, large scale industrial products have started to compete with features which are not relevant with respect to the operation of the product. Even the outlook of heavy machinery is being designed so that it can be used as an element of successful sales. In such cases laser color marking of stainless steel surfaces may be used for adding decorative features, which are not sensitive to corrosion, wear or scratches.

Constant decrease of fiber laser prices and simultaneous improvement in the technical features decreases the threshold of investing in laser marking. Even consumer product retailers may find it economically feasible to laser mark their products on site and personalize them with designs and colors favored by the customer. One big opportunity in laser color marking is being able to create RGB images by tailoring pulses to form colored pixels. In theory this is possible, but it presents a great challenge for the pulse stability, laser control and integration to scanners and other auxiliary equipment.

**Conclusion**

Laser color marking is a promising technique that has been known for several years. What is seen as a colored area is actually a reflective metal surface which is coated by a thin oxide film. The color is defined by the thickness of the oxide layer.

The process of laser color marking is an attractive alternative for printing, anodizing, emulsion coatings or using stickers. It does not use chemicals or tools, the accuracy is extremely good and different colors and figures can be marked just by changing the laser parameters and modifying the image using proper software. Use of the process is still limited, possibly due to the lack of information about the corrosion, wear and scratch properties of the surfaces.

MOPA fiber lasers offer an applicable tool for color marking. The vast parameter space and the possibility to independently adjust each laser parameter makes it possible to optimize the process to produce brighter, higher contrast colors. It could also be possible to take the viewing angle into account during the design process.

The processing results show that the main limiting factors for producing high quality markings are the pulse energy and pulse peak power. Using pulse width adjustable MOPA fiber lasers makes it possible to select a correct pulse energy for the material and then adjust the peak power by optimizing the pulse width. It should however be noted that finding correct processing parameters to create a certain color can be time consuming and some of the effects do not behave in a linear manner. But once the parameter combination is found, marking is reliable and effortless.

In order to find more industrial applications the process has to be made faster. This can be accomplished by using higher laser power, higher repetition rates and scanning velocities. It is also possible to do the marking in an oxygen atmosphere to enhance oxide film growth rate. A larger spot size makes it possible to use higher pulse energies still maintaining a feasible intensity on the surface. Instead of using a Gaussian beam profile, the single mode beam can be converted into a top hat beam, creating a more uniform intensity distribution, which might be beneficial for the outcome.

Over all it can be concluded that laser color marking has high potential to become a widely used technique for product marking and decoration. However, before the technique can be used in high volume consumer products, more research
and application tests are needed to establish and quantify the optical, wear, corrosion and scratch properties of the marked surface. It is also essential to create more information on how selected colors relate to the processing parameters on a given laser system.

References


