Color Marking of Stainless Steel and Titanium with the Laser Oxidation Method

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Abstract. Marking of metal products is essential in many industrial processes. It is mandatory for the finished products according to regulations of the European and world legislation. Traditional marking usually creates contrasting symbols that can easily be erased and forged. In recent years, a new method for product identification has appeared - color marking. One of the advantages of this method is that it is difficult to counterfeit. This article aims to present the progress of color marking technology on two types of materials. Three groups of factors have been analyzed: the laser source; the technological process; material properties. Their role in obtaining a specific color marking on Ti and AISI 304 is shown. The results are presented in tables. Each color can be repeated only with strict observance of the three groups of factors.

Keywords: Color, Laser Oxidation method, Marking.

1. INTRODUCTION

Marking of machines, assemblies and parts is mandatory during the modern manufacturing process. Products on the market must be marked as required by European legislation [1].

Laser marking of parts and components is essential for the aviation, automotive, medical and other industries.

Individual marking is necessary for automatic reading of information and tracking the quality of the details during the technological process. Monochrome laser marking is widely used in production which does not provide the necessary reliable protection against counterfeiting.

Laser color marking has many advantages: non-contact, flexibility, protection against forgery, minimal deformations after processing, good wear resistance, the possibility of color marking with high accuracy of the obtained image, environmental friendliness - a process without the use of chemicals [2]. It is necessary to improve the existing technologies, as well as to create new modern methods of laser color marking.

Color generation results from controlled surface oxidation of metal surfaces during the laser interaction[3]–[5]. This process needs further analysis and research.

This article reviews the development and methods of color marking on some metals. It is also presented how laser marking parameters affect the resulting colors on titanium and chromium nickel steel.
2. TRADITIONAL METHODS OF COLORING AND MARKING METAL SURFACES

Fig. 1. Block diagram of traditional methods of coloring metal.

a) Electrochemical oxidation (anodization) - obtained by electrochemical treatment in aqueous electrolytes (Fig.2). Anodizing requires high voltage and an electrolytic bath to carry out the process [6]. In these electrochemical processes, the change of metal ions in the electrolyte lead to different colors on the metal surface. The colors obtained in this technological process are limited [3], [7].

b) Thermal oxidation is a thermal process that takes place in thermal chambers. The essence of the method is the formation of an interference film on the surface of the metal, which has a different color [8] - [9].

c) Thermochemical oxidation occurs when the metal is heated in oxygen solutions containing, for example, H₂SO₄ and CrO₃ [10], [11]. The thermo-chemical method has a negative impact on the environment.

Electrochemical oxidation, thermal oxidation and thermochemical oxidation are one of the oldest industrial techniques [12]. However, the resulting films are characterized by structural weakness and the appearance of porosity, and additional processing is required to fix the colors [13].

Advantages of thermal and electrochemical technology are high performance on large areas and durability of the coating.

The disadvantages are the limited palette of colors, the inability to apply more than one color in one processing cycle. And the image has a low resolution and requires a pre-made template. Some of the listed disadvantages find their solution in thermal printing, screen printing and ink-jet printing.

Thermal printing, colored ink-jet printing, screen printing and others are techniques for applying colored logos and markings on metal parts. Their advantage is the wide variety of colors and their accurate reproduction, as well as the high resolution of the marking compared to thermal and thermochemical processing of metal parts. A significant disadvantage is the fading of the colors and the low wear resistance of these coatings [3].

3. LASER COLOR MARKING OF METALS.

Laser color marking is possible via the interaction of the laser beam with the surface of the metal. This interaction can lead to obtaining different colorings, which depend on: the type of laser, the parameters of the process, the type of treated material. Marking can be applied for informative or decorative purposes in the form of colored texts, logos, barcodes or data matrix codes [14], [15].

The high resolution of the applied marking is due to the small diameter of the laser spot around 13 to 60 µm [3], [14]. After the laser impact on the material, there is no need for additional technological treatments. Laser colored surfaces have good wear resistance and corrosion resistance, which is researched by [6], [15], [16].

The materials on which this scientific research has been carried out are chrome-nickel and titanium. They are used in the food industry and medicine.


4. LASER COLORING METHODS

a) Laser oxidation is a method of coloring metal surfaces, in which laser heating leads to the formation of a transparent or translucent oxide film [24], [25]. Light falling on the surface of the sample is reflected by the surface oxide layer, and coloration is observed in the treated areas.

b) Laser-induced periodic surface structures (LIPSS) are produced on the sample by impact using ultrashort pulses from femto or picosecond lasers [26], [27]. Typically, LIPSS have a period close to the laser wavelength and are oriented perpendicular to the polarization of the incident laser beam to metal samples. LIPSS generated colors are highly dependent on viewing angle. They were first described by Birnbaum on semiconductor materials using a ruby laser [28]. LIPSS method coloring of Silver are shown in Fig.3.
c) Surface plasmon resonance (SPR) is the third surface coloring method. The coloring is due to metal nanostructures and nanoparticles on the surface of the specimen. Unlike LIPSS, the colors observed with SPR are randomly distributed and do not change with viewing angle.

Lehmuskero [14] reported the formation of small areas of different coloration, which is due to areas of small color pixels that form as different color patches. This effect is due to different thicknesses of the oxide layer. Such coloring was achieved on chrome-nickel by heating the surface with a laser. Ackerl et.al [21] investigated laser marking and coloring of Ti-6Al-4V with ultrashort pulses. He introduces the chromaticity coefficient, which makes it possible to determine the parameters of laser processing to obtain the required color of the titanium surface. It should be noted that the same color can be achieved with different combinations of laser marking process parameters [18].

5. ADVANTAGES OF LASER MARKING USING THE OXIDATION METHOD

Laser color marking using the thermal oxidation method makes it possible to obtain several colors on one part. Other important advantages of the method are non-contact, direct marking of the products, minimal heat affected area, short duration of the impact, reduced processing costs, high processing speed and environmental friendliness. Advantages of the laser method compared to the traditional one are lack of tool wear, high degree of automation, free programming with different signs and symbols [2]. Laser color marking technology provides better copy protection, wear-resistant colors that do not fade over time. The small diameter of the laser spot $d_0 = 12 \div 65 \mu m$ makes it possible to obtain high-resolution markings and images on small areas.

6. COLOR LASER MARKING REQUIRED EQUIPMENT AND PARAMETERS

The equipment used for color laser marking are pulsed UV, Nd:YAG and Fiber lasers. To ensure the necessary relative movement of the laser beam on the sample, two galvanometer-controlled scanning mirrors are used to deflect the beam. Beam focusing is performed by an F-Theta lens with a 160 mm - 240 mm focal length. Schematic diagram of a laser system [22] is shown in Fig. 4.

There are different surface treatment strategies to obtain color markings in terms of line overlap and laser beam scanning speed. In this study, we focus on two of them. In the first strategy, the scan speed should be high $v \in [400, 1550] \text{ mm/s}$, in order to have a uniform distribution of heat on the surface, the distance between the lines must be small enough $\Delta x \in [4, 6] \mu m$ to provide sufficient energy for oxide formation [23] as seen in Fig. 5a.

The second strategy is achieved through relatively low speed $v \in [66, 205] \text{ mm/s}$ per scan and large line spacing $\Delta x \in [50, 100] \mu m$, as seen in Fig. 5b. In this strategy, the overall appearance is a combination of two colors (photos in Fig. 5b) while one of them comes from the melting zone, the other is from the heat-affected zone, due to heat dissipation.

The studied parameters for laser color marking are the average power of the laser beam in the range $P_c \in [3, 30] \text{ W}$, the scan rate in the interval $v \in [60, 850] \text{ mm/s}$, the scan step in the interval $\Delta x \in [10, 50] \mu m$, the frequency of the pulse in the interval $\Delta v \in [10, 50] \text{ kHz}$, the size of the laser spot and the pulse duration.

The change of these parameters leads to a different energy that affects the product and hence to a different coloring of the marked surface. The parameters of the laser and the technological process affect the chemical or phase composition of the marked surface and its morphology. These parameters also determine the quality of laser marking - contrast, wear resistance and corrosion resistance of the marked surface [23].
7. THE FACTORS AFFECTING COLOR MARKING

The influence of various factors on the creation of color during laser thermal oxidation is shown in Fig. 6.

They are three characteristic groups: related to the properties of the material; associated with the laser source; related to the technological process; the properties of the material. To them must be added the factors - overlap coefficient and volumetric density of the absorbed energy.

a) Parameters of the laser source

Laser marking of metal parts and products is mainly based on the use of solid-state (Nd:YAG) and fiber lasers with an average power of 10 W - 30 W. These lasers work in the UV to IR range with the wavelength of 553 ns - 1064 nm with the duration of the pulses according to different authors varying from \( \tau \in [13, 200] \) ns and frequency repetition rate interval \( v \in [20, 100] \) kHz. From the conducted studies, no research related to the influence can be found of the pulse duration on the resulting color. It is necessary to study this process because the duration of the pulse affects the pulse power, which is important in the formation of color on the metal surface.

The selection of the laser source is important for the implementation of the technological process of color laser marking. To achieve color reproducibility in marking, it is necessary for the laser source to have parameter stability throughout the exposure time and the ability to control the parameters [18]. In the process of color laser marking by the oxidation method, the following laser sources are used: Nd:YAG laser [20], [23], [31], [32]; Fiber laser [15], [16], [22], [30]; UV laser [3], which are reported in the papers mentioned above.

Fiber lasers are preferred for metal marking due to the low cost of laser systems, the high quality of the radiation, the low maintenance costs and their serial production.

Laser sources differ in wavelength depending on their type. Common lasers for marking are displayed in Table 1. Important for the oxidation color laser marking process is the wavelength to have good absorption by the material.

It can be seen from the table that the selected lasers mostly have a wavelength of \( \lambda = 1064 \) nm.

Power is one of the important parameters to achieve color laser marking because it is related to power density.

b) Parameters of the technological process

Marking speed is a basic parameter of the technological process. The time of impact on the sample depends on it, and hence the energy absorbed in the material in the impact zone. The authors [6], [14], [15], [16], [18], [20], [23] have investigated how the speed change affects the resulting color marking. A higher scanning speed leads to a lower surface temperature, which affects the color of the oxide film obtained on the surface of the metal [3].
Focus-defocus. When the laser beam affects the material, three cases are possible: focusing on the surface of the material; defocus below the surface and defocus above the surface of the processed material. The authors [3], [14] work in focus mode. In this mode, the diameter of the focal spot is around [13 – 47] µm. The material in this mode absorbs a large amount of energy. In this processing, the laser spot has the smallest diameter of the three cases, and the highest temperature can be achieved at the processing site. The authors [3], [6] use defocusing under the surface of the material. As the defocus increases, the diameter d of the working spot also increases, thereby reducing the energy with which the material is processed. The dependence of the spot diameter is inversely proportional to the power density \( q_s \) of the laser radiation. It follows that the absorbed energy very rapidly decreases with increasing defocus. This dependence was investigated by the authors [6] and is shown in Fig. 8.

Coloring is obtained by using different defocus values and the same laser average power. The horizontal color bar in Fig. 8 shows how the color saturation and its gamut change at different defocus values.

The step between the laser lines in the studies of [23] show that the colors are very sensitive to the step value (hatching) and even a small change in the value of the step causes a change in the color of the titanium surfaces. A larger step between the lines results in a smaller temperature affected zone.

The number of repetitions is discussed in details by [3]. He reported that the oxide layer grew rapidly in the first and second laser passes. Growth slows down in the third and subsequent passes, which coincide with the formation of microcracks at the oxide-base metal border.

After two laser scans at a speed of 500 mm/s, a gradual smoothing of the surface was observed with the polishing increasing as the number of passes increased. The oxide growth rate decreases with the number of laser passes and their thickness tends to stabilize, due to the diffusion of Fe into the oxide layer.

c) Complex factors affecting the process of color laser marking by the oxidation method are:

The overlap coefficient, which gives a relationship between marking speed, laser radiation power density and pulse repetition rate. Veiko et al. considered the influence of this factor [18].

The density of absorbed energy, which is related to pulse repetition frequency, laser radiation power density, marking speed, absorption capacity of the material, etc. Volumetric energy density and its characteristics have not been extensively researched for the color laser marking process.

Table 2 shows how changing the parameters of the laser source and the technological process change the color of the surface by the method of thermal oxidation.
Table 2 Changing the parameters of the laser source and the technological process for changing the color of the surface by the method of thermal oxidation

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CONCLUSION

An increasing number of companies are interested in color laser marking and its implementation in industrial production. This technology proves its advantages and prevails over traditional laser marking. It is able to produce a palette of colors on metal surfaces. The resulting colors are sensitive to process parameters, environmental conditions and material properties. Further research is needed to improve color repeatability.

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REFERENCES