Optics and Lasers in Engineering 84 (2016) 37–43

Contents lists available at ScienceDirect

Optics and Lasers in Engineering

journal homepage: www.elsevier.com/locate/optlaseng

Compositional and micro-scratch analyses of laser induced colored surface of titanium

Erhan Akman [a,b,*], Ecem Cerkezoglu [b]

[a] University of Kocaeli, Faculty of Aeronautics and Astronautics, Department of Aircraft Electric and Electronic, 41285 Kocaeli, Turkey
[b] University of Kocaeli, Laser Technologies Research and Application Centre, 41275 Kocaeli, Turkey

ARTICLE INFO

Article history:
Received 16 November 2015
Received in revised form
8 February 2016
Accepted 25 March 2016
Available online 11 April 2016

Keywords:
Laser color marking
Laser material processing
Titanium oxidation
Micro-scratch test

ABSTRACT

Laser marking of metallic surface is a very important application for industry. It is revealed that controlled oxide layer generation above the treated surface leads to colored appearance of metals with interference effect. The oxide layer control is provided with laser and process parameters. In this study, different colors of the Grade 2 titanium samples have been obtained by varying the laser scanning speed. Chromaticity coordinates of the different color surface have been calculated from the reflectance spectrum of the samples. Compositional analyses have been performed using X-ray photoelectron spectroscopy and X-ray diffraction methods. To examine the mechanical properties of the surface, micro-scratch test has been applied to all the colored surfaces. Although delamination has been observed between two laser scanning speed as 950 mm/s and 450 mm/s, it can be said that the adhesion between the titanium substrate and the oxide coating is good.

1. Introduction

Marking of the surfaces is a very important application for the industry to identify the products [1]. There are many methods such as printing, emulsion coating and electrochemical treatment used for this purpose. But these methods exhibit scratching, fading of the colors with time and pattern limitation problems [2,3]. As in the many other areas of the industry such as welding, cutting and heat treatment etc., lasers also have been adapted to marking application [4]. In contrast to problems that arise in conventional methods, non-contact working, high repeatability, high scanning speed and high flexibility have allowed the laser to be preferred [4]. Studies on different materials during laser marking revealed that colored surface can also be achieved with laser on numerous metal and alloys such as Ti, V, Cu and stainless steel (SS) in air [5].

In conventional methods color appearance of the coating is usually attributed to the interference phenomena of the reflected white light from the both oxide and metal surface [6]. The resulting color spectrum via constructive (nd=$\lambda/2$, λ, $3\lambda/2$..) or destructive (nd=$\lambda/4$, $3\lambda/4$, $5\lambda/4$..) interference depends on the film properties such as thickness of the oxide layer, refractive index and the order of interference at a given beam light incidence angle [2,3].

Nevertheless, to create a proper model that explains the optical appearance of the laser induced color surface, lots of work has been done. Langlade et al. [7] have indicated that the thicknesses of the oxide layer are too large to impute the color appearances of the laser treated titanium surface for interference phenomena. Even though Pérez del Pino et al. [8] have observed several titanium oxides depending on the accumulated fluence, due to thin layer observed above the thick layer of some samples, they highlight light interference phenomena should not be ignored. In the study done by Adams et al. [9] using nanosecond fiber laser on grade 2 titanium, they have reported that coatings generally consist of three layers as from the top TiO_2, TiO and an inhomogeneous mixture of Ti, O and N respectively. Besides, they concluded that the coloration occurs as a result of the interference of incident white light reflected from the upper and lower boundaries of the TiO_2 capping layer with the underlying TiO acting as a metallic reflector. Skowroński et al. [10] have showed that, the TiO_2 layer form on the top surface of the layers also includes nitrogen although its atomic concentration does not climb over %2. After sputtering surface with Ar^+ ions other oxidation states become visible and also an increase has been observed in atomic concentration of the nitrogen. According to the results of Skowroński et al. [10] it has been emphasized that as to the optical behavior of oxynitride layer not only interference effect but also absorption effect should be taken into consideration in surface coloring.

There are lots of laser parameters as pulse energy, pulse duration, scanning speed, repetition rate and processing parameters such as hatching distance (distance between the parallel laser beam traces) and scan strategy to change the properties of oxide layer, herewith the color of surfaces [11]. Although this flexibility seems like an advantage to obtain different colors, the existence of too many

* Corresponding author.
E-mail address: erhan.akman@kocaeli.edu.tr (E. Akman).

http://dx.doi.org/10.1016/j.optlaseng.2016.03.026
0143-8166/

parameters reveals the reproducibility problems.

In addition to the studies held in order to determine the main reason on coloration of the surfaces, several studies have also been carried out to determine the effect of the parameters on coloration and the repeatability of the colors. Antonczak et al. have conducted studies using a nanosecond Yb:glass fiber laser on Stainless steel [3] and Titanium grade 2 alloy [11]. A large number of different colors have been obtained by changing the process parameters by the researcher in the studies. However, the results have showed that all the analyzed process parameters affect the reproducibility of the color obtained. Although assuming some parameters such as pulse duration, pulse repetition rate and hatching distance can be easily fixed, there are restrictions in the very limited ranges for the other parameters such as laser fluence, temperature of the material, etc. to reproduce the color.

When the mechanical damage possibility of the surface is considered, it is seen that durability is also important in laser color marking application as well as obtaining different color. Mechanical properties of the laser colored stainless steel surface have been investigated by Lawrence et al. using Nanoindentation method [12]. The researchers have reported that while deformation, fracture and electromechanical behavior of laser color stainless steel surface are controlled by the combine properties of oxide and substrate metal, oxide mechanical properties are dictated by film thickness. Furthermore, aging processes have been applied to the laser colored surface created on stainless steel by Antonczak et al. in order to determine the susceptibility [3]. In their study they have evaluated the surface using UV radiation and a salt spray test. According to their reports, while the UV radiation does not cause any visible changes, rust formation is observed on salt spray test. But, rust formation has been attributed to an inappropriate choice of steel grade by researchers.

Although there are very different reports on laser color marking, investigating optical and compositional properties of the surfaces, a few reports are available in the literature about the wear and scratch resistance of laser colored titanium surfaces. The aim of the present study is to analyze the scratch damage which is most likely to occur in use in addition to the compositional properties of the laser colored titanium surface.

2. Experimental

Surface coloring process was performed using pulsed fiber laser of 20 W maximum power. This laser operates 1064 nm wavelength with pulse duration of 200 ns and repetition rate range between 20 kHz and 100 kHz. To deflect the laser beam a galvanometric system was used together with a 160 mm focal length F-Theta lens to focus the laser beam. During surface treatment, plates were fixed 2 mm below the focal point of the F-Theta lens (line width of the laser beam on the surface is approximately 90 µm under these circumstances). The position of the samples at the z axis was aligned using a manual stage. In the experiment commercially available Grade 2 plates (chemical composition: Ti=99.2%, Fe=0.3 %max, O=0.25 %max, C=0.08 %max, N=0.03 %max, H=0.02 %max) were used. Surfaces were cleaned with normal acetone before the experiments. On the samples, an area of 4 mm × 4 mm was irradiated in air by scanning the surface line by line with parallel laser beam traces. In the experiment to change the oxide thickness laser scanning speed thereby fluencies was chosen as variable. During the experiment while the power and repetition rate were kept constant as 20 W and 80 kHz respectively, scanning speed was changed between 1550 mm/s (S1) and 150 mm/s (S15) with 100 mm/s decrements for 4 µm hatching distance.

In order to determine the oxide concentration depending on the laser scanning speed on the treated surfaces, high-resolution X-ray photoelectron spectroscopy (XPS) was realized. Since heating of the surface will be less compared to the frequent hatching distance, the hatching distance was selected as 100 µm for the samples prepared for the XPS analysis. The XRD analyses were carried out to define the different oxide phases on four different color surfaces.

For an unbiased evaluation of the color changes due to the change on oxide layer, colors were determined via reflection spectrum in the range of 400–900 nm using a spectrometer. High intensity fiber light source (color temperature T_C=3200 K) was used during the reflection spectrum measurement. Visual analysis of the surface was realized using optical microscope. U-25LBD (Light Blue Daylight) filter which turns the illumination light into daylight was used during the optical imaging.

CSM Micro Scratch Tester was used to examine the scratch resistance of the surfaces. Rockwell S-218 type indenter was used with a spherical diamond and a contact radius of 200 µm. Indenter is performed a pre-scratch under the load of 0.03 N to eliminate the surface roughness effect. Mechanically induced surface damages in the form of a scratch were introduced on the surface of the samples using loads at 5 N with a scratch velocity 6 mm/min and 3 mm scratch length. Scratch test was repeated three times for each sample. After the test, in order to determine scratch hardness and evaluate the delamination of the oxide coating due to the mechanical scratch, optical microscope images of the each sample were taken. Hardness of the surface was calculated as in reference [13].

3. Result and discussion

3.1. Optical properties of laser colored titanium surface

There are different surface processing strategies to obtain color surfaces in terms of overlapping of the line and the scanning speed of the laser beam in laser color marking application [14]. In this study we advert two of them. In the first strategy, while the scanning speed should be high enough to have uniform distribution of the heat on the surface, hatching distance has to be small enough to provide sufficient energy for oxide formation [14] as seen in Fig. 1a. The second strategy is achieved by a relatively low scanning speed and sparse hatching distance as seen Fig. 1b. In this strategy, overall appearance form combination of two colors (interior pictures of Fig. 1b) while one of them comes from melting area, the other one is from the heat affected zone due to heat dissipation (Fig. 1b).

Optical properties of the samples were determined via the examination of the reflection spectrum of the each colored area. Reflection characteristics versus wavelength for different colors and the optical microscope images of the surfaces are shown in Fig. 2. The reflectivity spectrum of an untreated Grade-2 sample is also included in Fig. 2a for reference.

Due to the rough surface of the untreated sample, the reflectivity is low compared to treated surface with high scanning speed samples as seen in Fig. 2a. At the constant power and the hatching distance, a decrease on the scanning speed led to a decrease in reflectance of the surfaces. This behavior can be attributed to the attenuation of the oxide films whose thickness has been increased with a decrease in the laser scanning speed [5,9].

The shapes of the reflection spectrums have not changed while the scanning speed has been decreased from 1550 mm/s to 850 mm/s, denote as S1 and S8 in Fig. 2a and b. This case interpreted by the Adams et al. as, as the thickness of the oxide layer is very thin so interference effects should not play a large role [5]. As seen in Fig. 2b, there is not an appreciable change in the color up to this speed. After this point, when the speed reduction has been resumed, peak formation with a broad minima and maxima has