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Ultrashort laser coloration on metallic coatings

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Abstract

This study reports on the fabrication of structural and intrinsic color from the oxide layer layers via ultrashort pulses on three different metallic coatings deposited on glass substrate. Surface modifications are tuned by adjusting laser fluence deposited on metallic coating. Thickness up to 0.4µm of titanium (Ti), and Chromium (Cr) were deposited on borosilicate substrates by physical vapor deposition. A comprehensive study of the physical and chemical measurements leading to the different appearance is presented. Different physical modifications, at micro and nanoscale levels, were identified depending on laser processing conditions. Uniform and repetitive color palette on Ti and Cr was developed by femtosecond pulses.

Keywords: Ultrashort laser pulses; metallic coatings; coloration; nanopatterns

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1. Introduction

The color is a valuable feature not only for the decorative purpose, but also for many applications such requires labeling some kind of product information, identification of metal product and its counterfeit protection. Laser technology is emerging as powerful, flexible and environment-friendly technology for marking/coloring process instead of conventional methods (painting or printing). Recently, color marking by laser processing without using any chemicals has emerged as a novel technology to create a controllable wide color palette on solid substrate surfaces.

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The most common approach for laser coloring is based on the atmospheric heating and ablation of a metal surface. It is based on the formation of oxide films on the metal surface using solid-state and fiber laser emitting at different wavelengths [Z.L. Li, et al., 2009, F. Torrent et al. 2013, E.H. Amara et al., 2015]. Color palette and the sequence of their formation is directly related to the material and the laser processing parameters. Veiko et al., 2015 reported the coloration of stainless-steel surface during exposure to fiber laser with pulses in the nanosecond range. Moreover, they developed a procedure to develop a complete color palette based on reflectance spectra dependence on laser processing parameters. Ocaña et al. 2016 analyzed the coloring process of titanium surfaces by nanosecond pulses. They obtained colors gold-yellow, blue and purple in a reproducible way in areas of a few mm^2. The study concluded that the laser coloration is the results of and interference effect in the grown Ti oxide layers that appears as results of a laser-controlled irradiation by scanning a surface.

In parallel, the use of Laser Induced Periodic Surface Structures (LIPSS) is gaining a great attention during last years for a wide range of applications: surface color marking [Bizi-Bandoki et al., 2010], manufacturing more efficient solar cells with nanostructured surface [Moening et al, 2010], improvement tribological behavior of metallic surfaces or generation of surfaces with wettability control [Cardoso et al., 2011, Bizi-Bandoki et al, 2011]. Nano-scale periodic structures generated under laser irradiation, so-called *ripples*, are mainly attributed to interference between the incident electromagnetic wave and the scattered waves [J. F. Young, et al., 1984]. For ultra-fast laser radiation, the periodicity among ripples is down to few hundred of nanometers and the structure shape are directly linked to the material and the polarization state of the incident wave. Focus on coloring applications, ripples generate optical diffractive effects which can be controllable as function of polarization orientation, pulse length and material properties [Dusser et al., 2009].

Most of the studies reported until now have studied the effect of different ranges of pulse lengths on the coloring effect on solid substrate surfaces (mainly metals) considering both approaches: thermal oxidation and ablative effects (LIPSS). However, few reports [Panjan et al., 2014] have analysed the effect of laser radiation on the coloring effects produced on metallic coatings with thickness less than 1µm.

The purpose of the research present here is to analyse laser coloring process on thin mellitic coatings by ultrashort pulses. The experimentation was focused on generating structural (ripples) and intrinsic colors (oxide layers) by tuning laser fluence on Ti and Cr coatings produced by physical vapour deposition on glass. The analysis of the coating modification was carried out by scanning electron microscope (SEM) and energy dispersive x-rays spectroscopy (EDS).

2. Experimental procedure

A Physical Vapor Deposition (PVD) system was used in order to produce the Ti and Cr coatings using cathodic arc evaporation (CAE) method in the laboratory KSA 500 system designed at Kenosistec equipped with two cathodic arcs (4 inch). The base pressure of the vacuum chamber was 5 x 10-4 Pa. Ultra-clear borosilicate glass (90 x 50 mm x 3.85mm) were considered as substrates. Prior to coating deposition, the substrates were subjected to 20 min of Ar plasma etching and 1 min of metal etching to remove surface contaminants and enhance the adhesion between substrate and the coating. Planetary-rotation system was used to obtain uniform deposition of evaporated film coating and 350 °C substrate temperature during depositions, while a bias potential of −50 V was applied on the substrate. The average current was set at 90 A for chromium target (99.99% purity) and 100 A for titanium grade 2 (99.99% purity). The working pressure was 1 Pa with a constant

50sccm argon flow for Ti and Cr coatings. The deposition time was adjusted to achieve coating thickness up to 0.4µm. Cross sections of Ti and Cr films deposited on silicon substrate were analyzed by scanning electron microscopy (SEM) to adjust the coating growth and thus the final coating thickness.

The study was performed by a femtosecond laser system with maximum average output power 60W infrared wavelength, beam quality factor M^2<1.1, tunable pulse length from 350fs to 10ps and repetition rates in the range of f= single short to 40MHz. The laser beam was guided by a galvanometric scan mirror that allows beam to be deflected. The laser beam was focused on the metallic coating through a 100mm telecentric focal length that provides a spot diameter around 25µm at the focal plane. Sample of materials used for coloring was placed on x-y stage while the focusing distance is adjusted by a controllable Z-axis. A block diagram of the setup is shown in Figure 1a.

Laser coloring of metallic coatings was made line-by-line scan of surface by sequence of laser pulses with an overlapping along the x and y axis at different laser power levels (Fig.1(b)). Two different marking approaches were considered: overlapped laser spots at the focal plane and at a defocusing distance of 1mm. Defocusing spot diameter or around 45µm was estimated based on the laser beam quality (M^2) and beam caustic provided by the focusing lens.

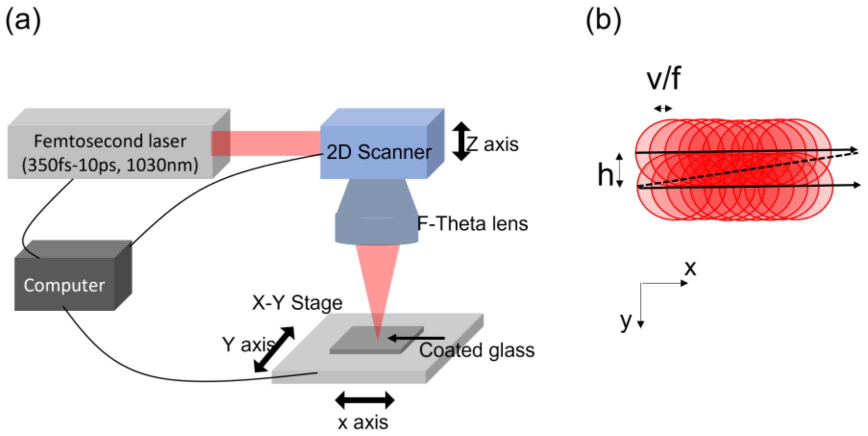

Fig. 1. (a) block diagram of the laser set up; (b) laser marking strategy.

For the two laser processing approaches pulse distance between consecutive pulses was fixed to 1.5µm that involves pulse overlap of 94% and 97% for defocusing and focusing approach respectively according to equation (1). For each approach, power level /energy per pulse and pulse overlap along y axis (h) were varied to find a proper laser parameter window that guarantees the coating treatment without removing it (table 1).

$$PO = \left(1 - \frac{v}{2w \times f}\right) \times 100 \qquad (1)$$

Where v represents the scanning speed, 2w the spot diameter and f the repetition rate.

As a first step, 3x3mm treated squares were generated for a wide range of laser fluences with the aim to narrow down the proper laser parameter window. Since glass substrate was considered in this study, an initial visual inspection provided enough information about the effect of laser radiation on the coating integrity. After that, selected laser fluences were applied on 20x20mm treated squared where characterization process was carried out.

Table 1. Range of laser parameters selected for laser coloring.

Marking strategy	Defocused	Focused
Spot diameter Φ [µm]	45	25
Frequency rate f [kHz]	250	2000
Average power P [W]	8-12	14-18
Marking speed v [m/s]	3	0,375
Hatching h [µm]	2.5- 20	1.25 - 5

Obtained samples were examined by means of scanning electron microscope (SEM) and energy dispersive X-ray spectroscopy (EDS) to assess the different effects that could define the color appearance of the laser treated coating. Element mapping was performed to characterize elemental composition and spatial distribution to understand possible changes in material composition after laser treatment.

3. Results

Fig. 2 discloses cross section of Ti coating deposited on silicon substrate by physical vapor deposition. Uniform coating thickness around 350nm was obtained after adjusting deposition parameters for both metallic coatings: Ti and Cr.

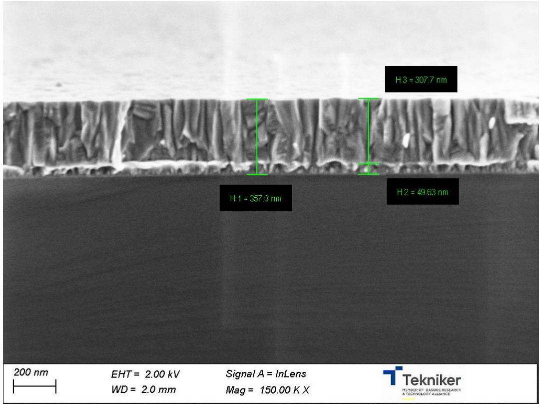

Fig. 2. Cross section Ti thickness coating on silicon substrate

Optimum laser fluence range to generate coloring effects on Ti and Cr coatings was experimentally defined. Table 1 gathers the selected laser parameters and fluence range that induce color change without coating removal. The assessment of proper parameter window was carried out by visual inspection to the transparent borosilicate thickness. The results evidence an increase in threshold spot fluence (just before coating removal) when h overlap increase. Spot fluence range and threshold fluence found for focused approach at 2000kHz (0.3mJ/mm2) were significantly lower than in the case of defocused approach (2mJ/mm2). The results suggest that, in the case of focused approach, the main mechanism for coloring is ablation. However, for defocused approach could be a mixture between ablative and thermal effects. Similar trends were identified for Cr coatings. However, Cr coating presented a higher sensitivity to laser fluence since laser parameters window required to generate coloring effects is narrow than in the case of Ti coating for both marking approaches.

Table 2. Process parameter window selected for coating coloring.

Coating	Ref.	f [kHz]	Ep[µJ]	v [mm/s]	h [µm]	Spot Fluence [mJ/mm2]
Ti	1	250	2.24	375	2.5	1.35
	2		2.64			1.60
	3		3.08			1.85
	4		2.24		5	1.35
	5		2.64			1.59
	6		3.08			1.85
	7		3.6			2.17
	8		2.64		20	1.59
	9		3.1			1.85
	10		3.6			2.17
	11		4.2			2.5
	12	2000	0.1	3000	1.25	0.23
	13		0.13			0.29
	14		0.13		5	0.29
	15		0.16			0.35
	16		0.2			0.43
Cr	17	250	2.64	375	2.5	1.59
	18		3.1			1.85
	19		4.16		20	2.5
	20	2000	0.195	3000	5	0.43
	21		0.235			0.52

Fig. 3 shows the most relevant experimental colors obtained in the case of Ti coating on glass substrate. Stable or intrinsic colors (Fig. 1(a)), which keep constant color appearance regardless of the viewing angle, were mainly obtained for defocused approach (f = 250kHz). In the case of focused approach (f = 2000 kHz) most of the coloring effects generated show a clear dependence with the viewing angle: structural colors. Fig. 1(b) exhibits the visual appearance of references 12 to 16 (Table 1) at two different viewing angles. Three set of laser parameters (references 10, 13 and 15) were applied on larger areas of 20x20mm (Fig. 1(c)) reaching significant repeatability and homogeneity. From a simple visual inspection, it is possible to anticipate two main mechanisms responsible for coating coloration: oxide film formation (intrinsic colors) and diffraction effect due to ripples fabrication (structural colors).

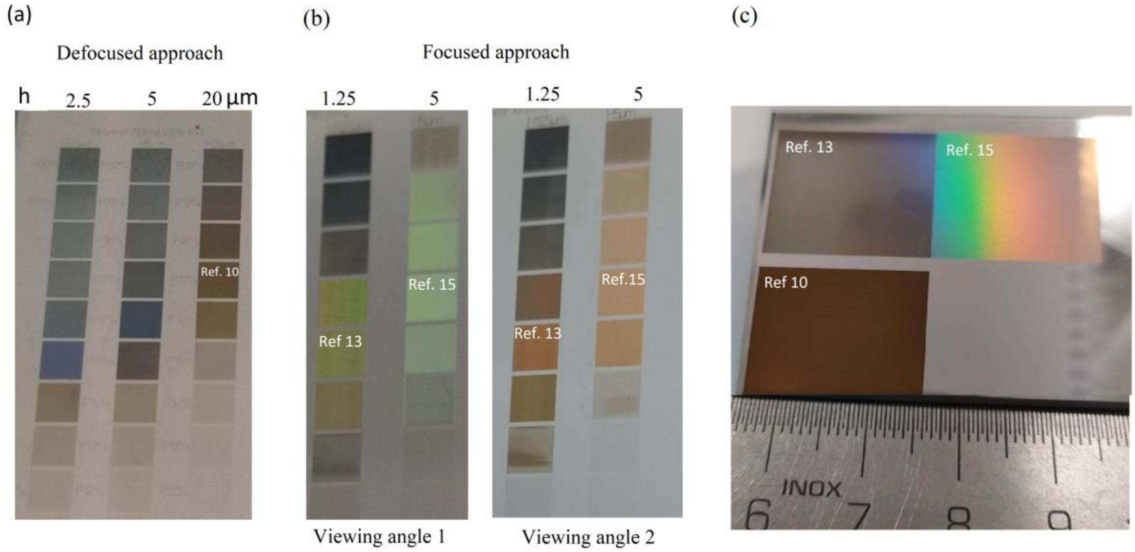

Fig. 3. Experimental colors induced on Ti coating on (a) small; (b) extended areas.

Fig. 4 (a), (b) and (c) show the morphological characterization of Ti coating surface before laser treatment and after laser treatment under conditions Ref. 10 and Ref. 15 respectively. In all cases Ti drops with typical diameters around 3µm are deposited on the coating surface with a random distribution. The latter effect is a direct consequence of cathodic arc deposition technique which involves the formation of macroparticles with sized in the range of 0.1-10µm in growing films. Fig. 4 (b), corresponding to defocused marking approach Ref. 10, displays the beginning of nanostructures generation with a ripples period around 400nm oriented perpendicular to the scanning direction (parallel y direction, Fig. 1(b)). Elemental mapping discloses the prensence of oxygen (red points) apart from additional elements from the substrate (Na, Si and Ca). In the case of color obtained for focused approach (Fig. 4(c), Ref. 15) the coating morphology reveals more clearly the presence of ripples in the same dimension range and direction than in the case of defocused approach. However, elemental mapping does not evidence the presente of oxygen on the treated titanium coating. In both cases, the elemental composition analysis indicates the existence of some typical elements from the borosilicate substrate (mainly Na, Ca and Si); however the absence of oxygen for color obtained by focused approach (Fig. 4(c), Ref. 15) suggests that the oxygen in the defocused approach comes from the coating surface. Thus, the results suggest that the intrinsic colors are mainly due to the oxide films formation by thermal effects, while in the case of strutural colors, nanostructures control the visual appearance. Intrinsic and structural colors where mainly found for defocused and focused approach respectively. Same trends were obtained in the case of Cr coating.

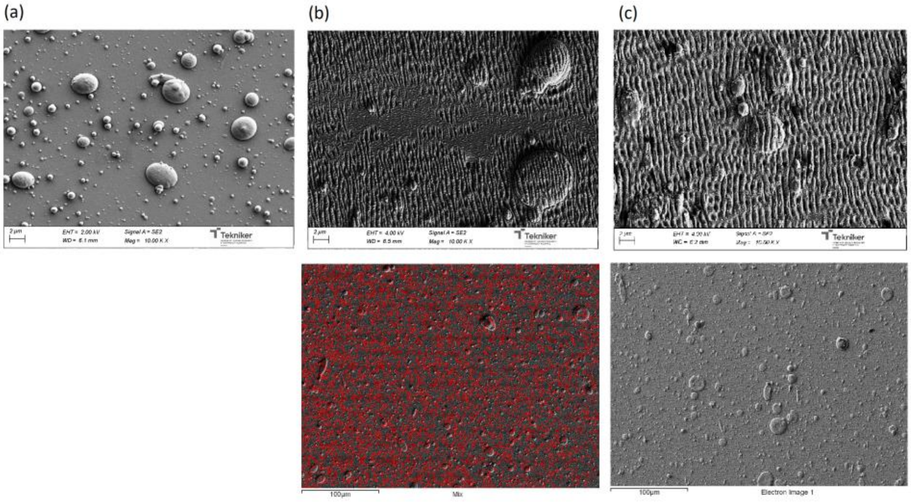

Fig. 4. SEM and EDS imagens of Ti coating (a) without laser treatment; (b) ref. 10 for defocused approach; (c) ref. 15 for focused approach.

Further investigations are in progress to analyze the correlation between the marking approach and the main mechanism responsible for coating coloring. In this regard, the identification of presence of oxide layer at the coating surface plays an important role to understand the interference effects, both among thin oxide layers and among nanostructures on the coating surface.

4. Conclusions

Titanium and Chromium coating thickness up to 0.4nm were deposited on borosilicate glass substrate by physical vapor deposition. Surface modifications were induced by ultrashort laser pulses on metallic coating adjusting fluence levels. Two color appearance were identified depending on the considered marking strategy: intrinsic or stable and structural colors. The first one was mainly related to thermal effects while structural colors were generated by interferences among ripples on the coating surface. Uniform and repetitive color palette on Ti and Cr was developed by femtosecond pulses.

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References

Amara, E.H., Haïd, F., Noukaz, A., 2015. Experimental investigations on fiber laser color marking of steels, Appl. Surf. Sci. 351, 1–12.

Bizi-Bandoki, P. , Benayoun, S., Valette, S., Beaugiraud, B. , Audouard, E., 2011. Modifications of roughness and wettability properties of metals induced by femtosecond laser treatment Appl. Surf. Sci., 257, pp. 5213-5218.

Cardoso, M.R. , Tribuzi, V., Balogh, D.T., Misoguti, L. , Mendonça, C.R., 2011. Laser microstructuring for fabricating superhydrophobic polymeric surfaces Appl. Surf. Sci., 257, pp. 3281-3284.

Dusser, B., Sagan, Z. , Soder, H., Faure, N., Colombier, J.P., Jourlin, M., E., 2010. Audouard Controlled nanostructrures formation by ultra fast laser pulses for color marking. Opt. Express, 18, pp. 2913-2924,

Li, Z.L., Zheng, H.Y., The, K.M., Liu, Y.C., Lim, G.C., Seng, H.L., 2009. Analysis of oxide formation induced by UV laser coloration of stainless steel, Appl. Surf. Sci. 256 ,1582–1588,

Moening, J.P. , Georgiev, D.G.. 2010. Formation of conical silicon tips with nanoscale sharpness by localized laser irradiation J. Appl. Phys., 107

Ocaña, R., Calatayud, A., 2016. Laser-induced Coloring on Small Titanium Surfaces. Physics Procedia 83, 225-232.

Panjan, M., Klanjšek Gunde, M., Panjana, P., Čekada, M, 2014. Designing the color of AlTin hard coating through interference effect. Surface & Coating Technology 254, 65-72.

Torrent, F., Lavisse, L., Berger, P., Jouvard, J.-M., Andrzejewski, H., Pillon, G., 2013. Wavelength influence on nitrogen insertion into titanium by nanosecond pulsed laser irradiation in air, Appl. Surf. Sci. 278 , 245–249,

Veiko, V., Odintsova, G., Gorbunova, E., Ageev, E., Shimko, A., Karlagina, Y., Andreeva, Y., 2016. Development of complete color palette based on spectrophtometric measurements of steel oxidation results for enhancement of color laser marking technology. Material and Design 89 , 684-688.

Young, J. F., Sipe, J. E., van Driel, H. M., 1984. Laser-induced periodic surface structure. III. Fluence regimes, the role of feedback, and details of the induced topography in germanium. Phys. Rev. B 30(4), 2001–2015.