Optics and Lasers in Engineering 108 (2018) 78–86

Contents lists available at ScienceDirect

Optics and Lasers in Engineering

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

# Grey scale promoted through laser ablation onto phosphate coated zinc commercial plates

F. Rey-García[a,*], F.M. Costa[a], A.J.S. Fernandes[a], F.J. Oliveira[b], L. Rino[a], C. Bao-Varela[c]

[a] Departamento de Física & I3N, Universidade de Aveiro, 3810-193 Aveiro, Portugal
[b] CICECO, Department of Materials and Ceramic Engineering, Universidade de Aveiro, 3810-193 Aveiro, Portugal
[c] UA Microóptica & Óptica GRIN, Photonics4 life group, Facultade de Física e Facultade de Óptica e Optometría, Universidade Santiago Compostela, 15782 Santiago de Compostela, Spain

ARTICLE INFO

*Keywords:*
Zinc
Laser ablation
Surface processing
Decorative coatings
Grey scale

ABSTRACT

Phosphate coated zinc commercial plates (Anthra-Zinc®) have been processed by laser ablation in the nanosecond pulsed regime varying the repetition rate at 10, 20 and 50 kHz. Phosphate coating was completely characterized. By monitoring the fluence it was possible to define three different processing regimes: phosphate ablation (up to 116 J/cm2), zinc ablation (up to 288 J/cm2) and zinc melting (at 375 J/cm2). 3D profilometry was used to assess both the roughness and depth parameters corresponding to each regime. The brightness was estimated from 450 to 800 nm by reflectance studies. Consequently, a long-lasting grey scale was attained envisaging in- and outdoor decorative uses.

## 1. Introduction

Zinc has excellent mechanical properties as castability, corrosion resistance or calenderability that make it interesting for industry [1,2]. In fact, together with its corresponding alloys, is one of the most employed metals for a wide range of applications as automobile components, construction, light industry, electrical applications, etc. [1–4]. Nowadays, its consumption among non-ferrous metals is only behind aluminum and copper [4]. On the other hand, Zn and corresponding alloys are widely employed as protective coatings in steel, stainless steel, iron or precious metals, among others, due to its corrosion resistance [1,4–8]. The protection process basically consists on the formation of corrosion zinc products that act as barrier coating to ambient conditions [1,4]. Galvanization is the most common name used by industry that refers to this process. However, there are different galvanizing techniques such as hot-dip galvanization (HDG) [8] and electroplating [9]. Pulsed laser deposition (PLD) [10] and phosphating [11–15], among others, are alternative coating techniques for this approach.

Phosphating is one of the most widely employed methods to improve corrosion protection on materials. Basically, this process consists in the reaction between metal substrate ions and mineral acids, such as nitric and phosphoric, used to dissolve them to form, after pH increase, the crystalline zinc phosphate coating, as Donofrio [13] reported in detail. Sometimes, organic coatings such as epoxy resins are post-deposited to improve corrosion protection and/or to provide defined aesthetical aspects [14–16].

On the other hand, PLD has been also widely employed by researchers to obtain oriented Zn-based films, namely as a protective layer in components for energy transport applications [17–19]. Another example reported by Popescu et al. [18] refers to coated textile fibres with ZnO films to achieve super-hydrophobic surfaces. However, despite the large number of studies about Zn and Zn-based PLD, no studies can be found about the laser ablation effects on metal target, centering all foci on the developed coatings. Concerning laser ablation, this process modifies surfaces creating different micro- and nano-metric patterns [20,21], or changes the metal phase [22], usually provoking coloration effects [23]. For example, Rico et al. [22] have presented a new method for the fabrication of metal-like decorative layers on glazed ceramic tiles that, after laser treatment both in air and in vacuum varying the applied fluence, present green, yellow, cyan or brownish/redish colors. On the same way, Khafaji et al. [24] have recently obtained a palette of colors produced by nanosecond pulsed laser ablation of commercially pure titanium (grade II) plates under different processing atmospheres by mixing argon with different proportions of oxygen.

Thus, the aim of this work is to study the laser ablation at ambient conditions of commercial protected Zn plates in order to obtain a grey scale by varying different laser parameters including the applied laser fluence. Furthermore, the Zn employed here (AnthraZinc®) is coated with a black layer formed by zinc phosphate and an organic resin [15] that favors aesthetically the surface finish. As an additional effort, laser ablation was demonstrated to be a very suitable and ready option to be applied on industrial scale for this application [25].

* Corresponding author.
*E-mail address:* frgarcia@ua.pt (F. Rey-García).

https://doi.org/10.1016/j.optlaseng.2018.04.018
Received 10 February 2018; Received in revised form 29 March 2018; Accepted 29 April 2018
0143-8166/

**Table 1**
Laser parameters applied in each area of $5 \times 5$ mm$^2$. Tags 1, 2 and 3 in the name label correspond to a defined value of current applied for laser pulse generation.

| | Power (W) | Frequency (kHz) | Mark speed (mm/s) | Fluence (J/cm$^2$) | Pulse width (ns) | Irradiance (MW/cm$^2$) | Surface appearance |
|---|---|---|---|---|---|---|---|
| Zn1-10 | 3.73 | 10 | 100 | 211 | 50 | 4222 | brilliant |
| Zn1-20 | 4.12 | 20 | 200 | 116 | 85 | 1370 | brilliant (–) |
| Zn1-50 | 4.66 | 50 | 500 | 53 | 155 | 340 | dark |
| Zn2-10 | 5.09 | 10 | 100 | 288 | 45 | 6401 | brilliant (+) |
| Zn2-20 | 5.88 | 20 | 200 | 166 | 70 | 2377 | brilliant (-) |
| Zn2-50 | 6.52 | 50 | 500 | 74 | 135 | 546 | grey |
| Zn3-10 | 6.62 | 10 | 100 | 375 | 40 | 9365 | brilliant (++) |
| Zn3-20 | 7.65 | 20 | 200 | 216 | 60 | 3606 | brilliant (+) |
| Zn3-50 | 8.57 | 50 | 500 | 97 | 115 | 844 | grey (+) |

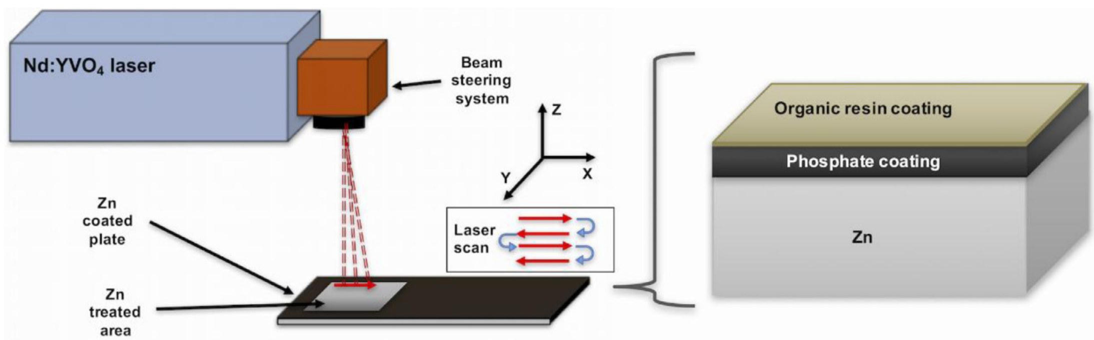


**Fig. 1.** Laser ablation scheme and Zinc phosphated commercial plate (Anthra-Zinc®) layers structure.

The morphology, microstructure and composition of both the pristine coating and the laser treated areas were achieved by Scanning Electron Microscopy (SEM) coupled to X-Ray spectroscopy (EDS), X-Ray diffraction (XRD) and µ-Raman spectroscopy. The topographic characterization was completed through optical profilometry. The brightness modification promoted by laser processing that allows achieving a grey scale was studied by optical reflectance spectroscopy.

## 2. Materials and methods

### *2.1. Materials*

Zinc phosphated commercial plates from Anthra-Zinc® [15] were employed in this work. The black plates of 1 mm thickness and coated in both faces are used for building facades promoting together protection and aesthetically enhancement.

### *2.2. Experimental: laser ablation*

Zinc phosphated plates were treated with a quasi-perpendicular diode-pumped solid-state Nd: $YVO_4$ laser (Powerline E20, Rofin) emitting at 1064 nm on nanosecond pulsed regime at repetition rates between 10 to 50 kHz (Table 1). Tags 1, 2 and 3 in the name label correspond to a defined value of current applied for laser pulse generation. The laser apparatus is fitted with a galvanometer beam steering system and a flat-field lens of 160 mm focal distance given a spot size ca. 15 µm that allows scanning the substrate within the XY plane [26]. A matrix of different laser parameters was designed by software (Rofin CAD-like software) in order to irradiate areas of $5 \times 5$ mm$^2$ (Fig. 1). Both frequencies as marking speeds were selected aiming to promote maxima pulses and scanning overlapping ratios that allows a continuous processing along the XY plane [22,26–28]. Pulse width is modulated by equipment [29] from frequencies and power selected for experiments. In addition, pulse width decreases with fluence aiming to favor physical processes, namely evaporation of species, and reducing photothermal effects [30,31]. Thus, the laser parameters were designed to regulate fluence increasing and, also achieving the maximum surface scanning ratio trying to avoid both the longitudinal features typical of ablation processes [32,33] and the thermal effects commented above. Indeed, this sequential approach usually minimizes the laser processing thermal effects on the material [27]. This point was considered crucial in this work to promote pure ablation effects since Zn possess a melting point (420º C) [34] lower than Al (660º C), Cu (1083º C), Cu/Zn (~900º C) or Ti (1680º C), among others. All those metals have been processed by laser ablation and widely studied [27,33,35-39].

### *2.3. Morphological characterization*

The surface of the irradiated areas was characterized by scanning electron microscopy (SEM, TESCAN Vega 3 SEM) fitted with energy dispersive X-ray spectroscopy (EDS). Room temperature (RT) µ-Raman spectroscopy measurements, using the 441.6 nm line of an external He–Cd laser (Kimmon IK Series) and the 633 nm line of an internal He-Ne laser, were also performed to corroborate the compositional analysis. A Horiba Jobin-Yvon HR800 instrument fitted with a 100x magnification lens with numerical aperture 0.9 and a minimum spot size < 2 µm was employed to conduct these studies.

The surface topography was assessed, enabling the measurement of the roughness (Ra) and the depth (Z) in each area using a non-contact 3D optical profiler (S neox® 3D, Sensofar) provided with a high-resolution CCD sensor of up to $1360 \times 1024$ pixels in combination with high-resolution displays of $2560 \times 1440$. The bright field mode used a 10x objective with numerical aperture (NA) 0.30 having an optical resolution in XY of 3 nm and a vertical resolution (Z) of 25 nm. On the other hand, interferometric analysis was performed through a 100x objective with 0.90 of numerical aperture, having optical (XY) and vertical (Z) resolution values of 0.15 µm and 1 nm, respectively.

### *2.4. Optical characterization*

The optical reflectance was estimated with an USB4000 Ocean Optics spectrometer (fitted with a 600 gr and a 25 µm slit) coupled to a 600