Environment. Technology. Resources. Rezekne, Latvia
Proceedings of the 13th International Scientific and Practical Conference. Volume 3, 242-244

Optical Properties of Laser-Colouring Marked Stainless Steel

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Abstract **- Laser colour-marking method often displace conventional marking techniques. Complicated technology of laser-induced periodic surface structure creation on stainless steel samples allows changing their surface morphology and optical properties, which were studied in this work by atomic force microscopy (AFM), laser scanning microscopy, reflectance spectroscopy and ellipsometry. Reflectance spectra of the samples demonstrate reflectance maxima correlate with the visible colours of the samples and with the extrema in the non-monotonic spectral dependences of the derivative of real part of complex dielectric permittivity extracted from the ellipsometric data. Thus, the most intensive light scattering takes place when the real part of complex dielectric permittivity falls down quickly with changing wavelength. We did not observe any "azimuth anisotropy" in our optical measurements at constant incidence angle: the spectra were the same independently of the light incidence plane orientation (parallel or perpendicular to the previous laser light spot scanning direction). We suppose that this selective resonance-like light scattering is due to the sample surface inhomogeneity, which is the result of previous laser treatment. This assumption agrees with estimations based on laser microscope and AFM images as well as with predictions of Mie theory. Thus, the colours of the samples under study are due to the light scattering by randomly distributed surface species with different sizes.**

Keywords - laser colour-marking, stainless steel, optical properties.

I. INTRODUCTION

Two main methods of laser colouring of metals are mentioned in the literature [1]. The first one utilizes a laser as a heat source, which fabricates a transparent or semitransparent oxide film on the metal surface. White light illuminating the sample is reflected from the surface of both the oxide and metal. As a result of interference of the reflected light beams, a colour effect can be obtained. The thickness of the oxide layer, its refractive index, and the order of interference determine the colour spectrum. If one uses the second method, colour can be obtained on the metal surface by the formation of laser-induced periodic surface structures (LIPSS), acting as diffraction gratings.

Our experimental results demonstrate one more additional reason for colour appearance on the metal surface after laser treatment: the colours of the sample may be due to the light scattering by randomly distributed surface species with different sizes.

II. MATERIALS AND METHODS

We used the samples of stainless steel with dimensions of 100 × 100 mm and thickness of 1 mm. Before the experiment, the plates were washed with isopropyl alcohol in an ultrasonic cleaner. The samples were marked in atmospheric air with the help of industrial laser marking system „DFL Ventus Marker II" (Firma ACI). Fiber laser with wavelength 1062 nm, average output power 20 W,

Online ISSN 2256-070X
https://doi.org/10.17770/etr2021vol3.6516

Published by Rezekne Academy of Technologies.

pulse peak power 12 kW, variable pulse duration and pulse frequency 1-1000 kHz was used. Details of the sample preparation have been described in [2], [3].

AFM images were obtained by scanning probe microscope «NanoEducator». Surface morphology was also studied by KEYENCE 3D Laser Scanning Microscope VK-X100/X200.

Angular resolved reflectance spectra $R(\lambda)$ of the samples under study were measured under illumination by unpolarized white light from a tungsten lamp using a collimated beam. Reflected light was analyzed by USB650 Red Tide spectrometer (Ocean Optics, Inc.).

Ellipsometry determines the change in polarization of reflected light from a sample by measuring two parameters Ψ and Δ that characterize the relative change in the amplitudes of the *p*- and *s*- polarized waves and the phase shift between them:

$$\exp(i\Delta)\tan\Psi = \frac{R_p}{R_s},$$

where R_p and R_s are the reflection coefficients.

After these measurements of ellipsometric parameters, one can carry out calculations of important physical characteristics (refractive index *n*, extinction coefficient *k*, real (ε') and imaginary (ε'') parts of complex dielectric permittivity etc.) of the sample using Fresnel formulae [4] and some theoretical models (semi-infinite effective medium is the simplest one).

In this work, we used spectroscopic ellipsometer "Ellips-1891", working at static photometric mode without any rotating elements or modulators [5].

III. RESULTS AND DISCUSSION

Reflectance spectra of the samples No. 2, 3, 4, 5 (having blue, green, orange and red colour, respectively) measured at the angle of light incidence $\theta = 50^0$ are shown in fig. 1. One can see rather wide reflectance bands with maxima at approximately 475, 570, 635 and 705 nm, respectively. The similar results correlating with the visible colours of the samples were obtained at the angle of light incidence $\theta = 30^0$ (fig. 2).

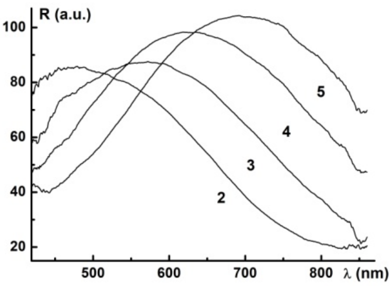

Fig. 1. Reflectance spectra of the samples No. 2, 3, 4 and 5 at the angle of light incidence $\theta = 50^0$.

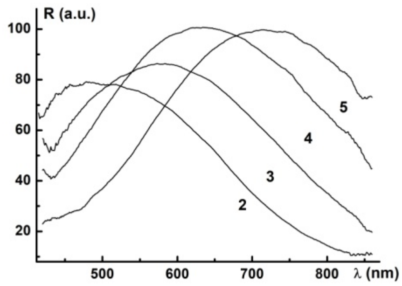

Fig. 2. Reflectance spectra of the samples No. 2, 3, 4 and 5 at the angle of light incidence $\theta = 30^0$.

Fig. 3 demonstrates spectral dependences of ellipsometric parameters Ψ and Δmeasured at the angle of light incidence $\theta = 50^0$ for one of the samples. It should be emphasized, that we did not observe any "azimuth anisotropy" in our optical measurements at constant angle of light incidence value: the spectra was almost the same independently of the plane of light incidence orientation (parallel or perpendicular to the previous laser light spot scanning direction) – see solid and dotted lines in fig. 3. Thus, the colours of the samples under study are not caused by the "diffraction grating effect".

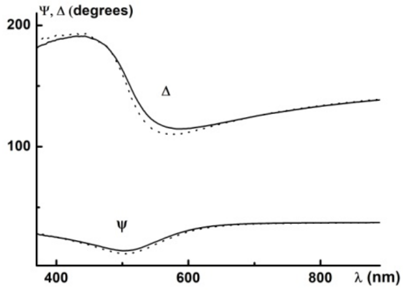

Fig. 3. Spectral dependences of ellipsometric parameters of the sample measured at the angle of light incidence $\theta = 50^0$. Solid and dotted lines correspond to the plane of light incidence orientation (parallel or perpendicular to the previous laser light spot scanning direction, respectively).

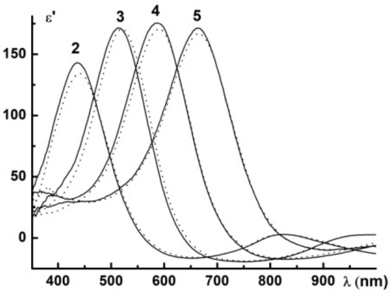

Fig. 4. Spectral dependences of the real part of complex dielectric permittivity ε' for the samples No. 2, 3, 4 and 5 measured at the angle of light incidence $\theta = 50^0$. Solid and dotted lines correspond to the plane of light incidence orientation (parallel or perpendicular to the previous laser light spot scanning direction, respectively).

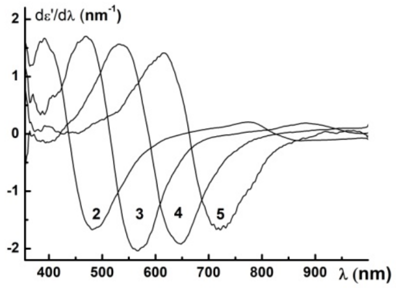

Fig. 5. Spectral dependences of the derivative of the real part of complex dielectric permittivity $d\varepsilon'(\lambda)/d\lambda$ for the samples No. 2, 3, 4 and 5 measured at the angle of light incidence $\theta = 50^0$.

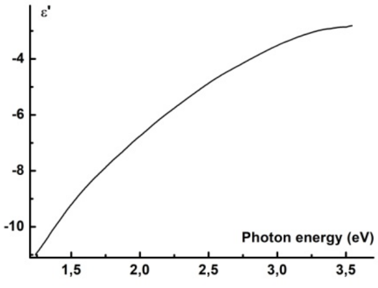

Fig. 6. Spectral dependence of the real part of complex dielectric permittivity ε' for the initial stainless steel (“substrate”) measured at the angle of light incidence $\theta = 70^0$.

Figs 4 and 5 show non-monotonic spectral dependences of the real part of complex dielectric permittivity ε' and those of its derivative $d\varepsilon'(\lambda)/d\lambda$ extracted from the ellipsometric data for the samples No. 2, 3, 4 and 5. Note that no extrema could be observed in the monotonic spectral dependence of the negative ε'value for the initial stainless steel (“substrate”) in the investigated intervals of photon energy and the angles of light incidence (see, e.g., graph in fig. 6 which is typical for metals [6]).

One can see that all the maxima positions in fig. 1 correspond with minima in fig. 5. Thus, the most intensive light scattering takes place when the real part of complex dielectric permittivity ε' value falls down very fast with changing wavelength λ. This behaviour is specific for dissipating systems, where significant dispersion of ε'value (usually near the resonance frequency) leads to energy dissipation, high dielectric losses etc.

We suppose that this selective resonance-like light scattering [4], [7] is caused by the sample surface inhomogeneity which, in its turn, may be the result of previous laser treatment [8]. Qualitative estimation based on laser microscope and AFM images [3] leads to the conclusion that the characteristic size of randomly distributed surface species increases with the sample number (from 2 to 5), correlating with the shift of the peculiarities in figures 1 and 5 to the longer wavelengths. This statement agrees with the predictions of Mie theory, concluding that scattering characteristics of spherical particles depend upon the non-dimensional parameter $q = 2\pi a/\lambda$ [4], [7], where $2a$ is the sphere diameter. From this point of view, particle size growth has to increase corresponding resonance scattering wavelength; this prediction is in consistency with our experimental results.

IV. CONCLUSIONS

Laser colouring of metal surface may be caused not only by interference in thin oxide films and/or by diffraction of light on laser-induced periodic surface structures. We suggest one more possible mechanism of colour laser marking: selective resonance-like light scattering due to the sample surface inhomogeneity, which is the result of previous laser treatment. This assumption agrees with optical data and estimations based on laser microscope and AFM images as well as with predictions of Mie theory. Thus, the colours of the stainless steel samples may be due to the light scattering by randomly distributed surface species with different sizes appeared after laser irradiation.

V. ACKNOWLEDGMENTS

The authors are grateful to Professor L. Lazov for choosing a research direction and helpful discussions.

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