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Laser coloration of metals in visual art and design

YA. M. ANDREEVA,[1] V. C. LUONG,[1] D. S. LUTOSHINA,[1] O. S. MEDVEDEV,[2] V. YU. MIKHAILOVSKII,[2] M. K. MOSKVIN,[1] G. V. ODINTSOVA,[1,*] V. V. ROMANOV,[1] N. N. SHCHEDRINA,[1] AND V. P. VEIKO[1]

[1]*ITMO University, 49 Kronverksky Pr., St.Petersburg 197101, Russia*
[2] *St. Petersburg State University, 7/9 Universitetskaya nab., St., Petersburg 199034, Russia*
**gvodintsova@corp.ifmo.ru*

Abstract: Visual art is an integral part of human life, which, like a mirror, reflects the lifestyle and capabilities of a generation. Moreover, each epoch contributes to the development of artistic expression techniques. In this article, we discuss three novel approaches to visual art and design from the point of view of modern photonics and laser technology. Laser methods of metal coloring are considered regarding their physical nature, and their ample opportunities for the creation of different artworks are demonstrated.

1. Introduction

Adherence Art is a chronicle of eras which keeps thoughts, hopes and values to be conserved for descendants. Every generation of every nation has contributed to the development of various art forms. Modern technologies give an opportunity for humanity to broaden ways of expression people's inner world through art. Nowadays science and art evolve interconnectedly. This fact led to the growing interest for such type of art as Science Art, which allows using standard materials and media in extraordinary ways.

One of the most popular materials for arts is metal due to its durability, toughness, and flexibility. Thus, there is an immense number of artworks made of different metals which have been continuously increasing since ancient times. Artists endeavor not only to reshape their metal works but also to change their colors. Therefore, different metal coloration techniques such as anodizing, electroplating, hot and cold enamel coating, powder coating [1–4] appeared. However, previously known methods tend to lose relevance. Since the technological progress has not bypassed this area of design, the old techniques are being supplanted by lasers providing comprehensive possibilities.

Laser coloration of metal surfaces provides a broad palette of colors, and the ability to control the result with very high accuracy to afford almost unlimited potential for creative work. Therefore, one can consider a laser as a brush; metal as a canvas, and surface structuring as paint.

There are several possible approaches to laser coloration of metals. One of the most successful and reliable methods is the color laser marking technology (CLM technology). The change of optical properties, i.e., the reflectance of the metal surface in the visible range occurs due to thin oxide films formation when exposed by radiation of fiber laser [5–7]. The thicknesses of such films as well as their composition are already studied both for stainless steel [8,9] and titanium [10]. But for visual arts, it is essential to control the quality, and colorimetric characteristics of the obtained surface, therefore the connection between processing temperature and resulting color have to be revealed. Here we study the temperature dependence of obtained colors and its relation with the thickness of oxide layer using titanium as an example.

It should be noted, that CLM technology cannot be applied to metals of poor reactivity with oxygen such as precious metals, while their coloration is highly important in jewelry art.

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The possible solution has been already suggested by the local laser oxidation of a titanium film sputtered on the silver and gold surface [11]. In this work, we present another approach based on metal nanoparticles formation at laser irradiation. The color, in this case, is related to surface plasmon resonance in these nanoparticles. Previously it has already shown that subwavelength nanostructures can be utilized for color marking [12] and information encoding [13]. Most often such nanoscale objects are produced by electron beam lithography [14] or thin film dewetting [15]. In this paper, we introduce the direct writing technique on massive silver using laser pulses of nanosecond duration. This method does not require additional sample preparation and can be utilized for pieces with complex shapes. The reflectance of the processed material depends on the composition, shape, and size of nanoparticles [16].

There is also another mechanism of laser coloration which is under discussion in this work. It is based on diffraction of light on periodic surface structures (PSS) which are produced because of interference between laser radiation and a surface electromagnetic wave. This method gives an opportunity to alter color depending on the viewing angle but also yields a possibility to protect masterpieces against counterfeiting [17–19].

Hence, the overall purpose of the work is to present a comprehensive study of novel laser-based approaches of Science Art and to highlights the several fold possibilities of laser technologies in visual art and design.

2. Results and discussion

One of the essential characteristics of visual art is color. An artist meticulously finds each color and tries to check all the shades before applying. From this perspective, an issue of color control for a novel artistic tool is critically important. In this work, we are suggesting using the fiber laser as the instrument for a new type of art thus there is a need to precisely manage the result. To provide the required spacious resolution the control of laser beam movements is carried out automatically by program code. Another question is how to provide exact color appearance.

For all the considered methods the temperature distribution is one uniform characteristic controlling the result. Thus, all the dependencies in the present article are expressed via the temperature after N pulses exposure, which corresponds to the multishot irradiation by rectangular light pulses with a uniformly distributed intensity in the spot and disregards the change of material reflectivity during exposure [5]:

$$T(x,t) = T_0 + \frac{2(1-R)I\sqrt{a}}{k}\sum_{m=0}^{N}\left[\sqrt{t-\frac{m}{f}}\cdot ierfc\left(\frac{x}{2\sqrt{a\left(t-\frac{m}{f}\right)}}\right) - \sqrt{t-\frac{m}{f}-\tau}\cdot ierfc\left(\frac{x}{2\sqrt{a\left(t-\frac{m}{f}-\tau\right)}}\right)\right] \quad (1)$$

where R – reflectivity (at λ = 1.06 μm); a – thermal diffusivity; k – thermal conductivity, I – intensity, τ – pulse duration, f – frequency.

2.1 Metal coloration by laser oxidation of the surface

Metal coloration by laser oxidation of the surface will be considered on the example of titanium. A multilayer oxide film is formed due to laser exposure in the air on the titanium surface, as shown in Fig. 1(a). The resulted color is determined both by interference effects in the upper oxide layer (TiO_2), as illustrated in Fig. 1(b) and the intrinsic color of the lower oxide layers (Ti_2O_3, TiO) [20].

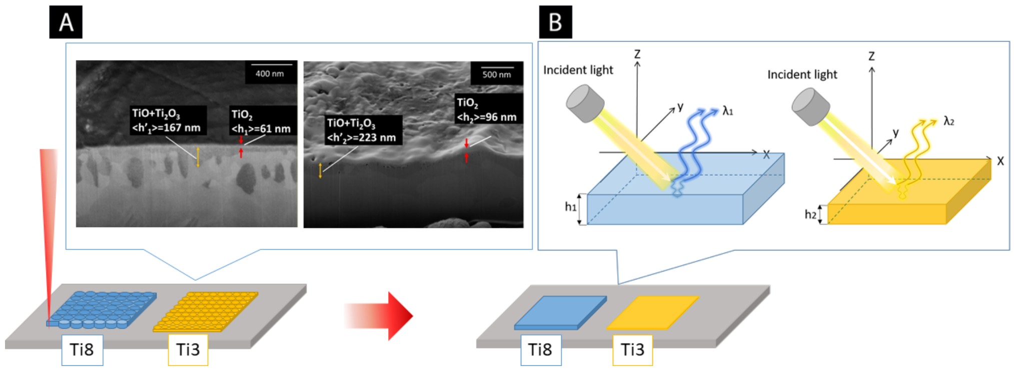

Fig. 1. Line-by-line formation of multilayer oxide film on titanium surface due to the laser exposure: SEM images (cross section) of the titanium samples Ti8 and Ti3 heated to a temperature of 2150 K and 1850 K, correspondingly, (A); the process of light interference in the upper oxide layer of TiO2 (B).

To obtain the desired color, complex oxide film must keep a certain thickness. This can be achieved by the control of exposure temperature. Figure 2(b) shows the temperature ranges (1700 K - 2300 K) where colors are formed on titanium and the Lab color coordinates of the samples. Reflection spectra of every obtained sample were measured, and colorimetric characteristics were calculated in accordance with CIE 2000, as can be seen in Fig. 2(a). Each specific color was designated as such where the color difference is more than 10. According to the taken criterion, this overall range can be divided into nine different colors. Oxide film's thickness increases with the rise of the temperature [5], and it leads to the shift of the reflection minimum to the infrared range of the spectrum. Visually one can observe that colors change from light yellow to brown and then converts into blue shades.

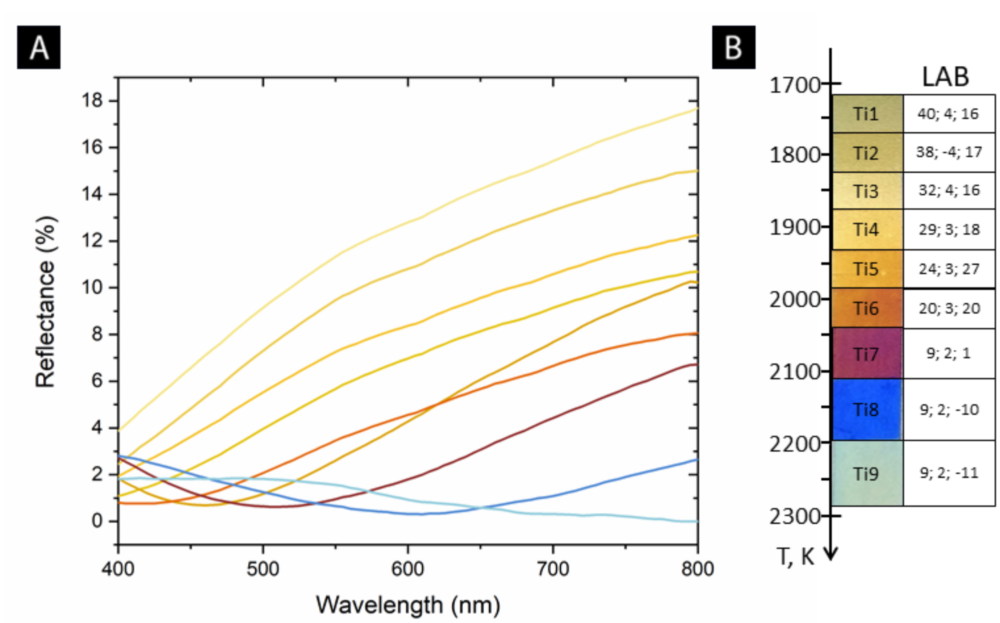

Fig. 2. Reflection spectra of a titanium surface after laser exposure (A), the temperature range for obtaining colors (colors of reflectance spectra corresponds to LAB coordinates colors) on titanium and the Lab color coordinates of the samples (B).

Therefore, with the well-determined color dependence, we can control colors with very high precision. Productivity is one of the most important characteristics of any technology.

Scanning speed for CLM usually does not exceed the value of 0.5 cm^2/min [5,7,10]. In this work, we achieved the value of 1.4 cm^2/min using marking modes with high pulse repetition rates (up to 1000 kHz).

Figure 3(a) shows an illustration for Air France magazine by artist Tom Haugomat produced on the surface of titanium using the obtained palette (treatment time is 14 min). Figure 3(b) shows the original picture.

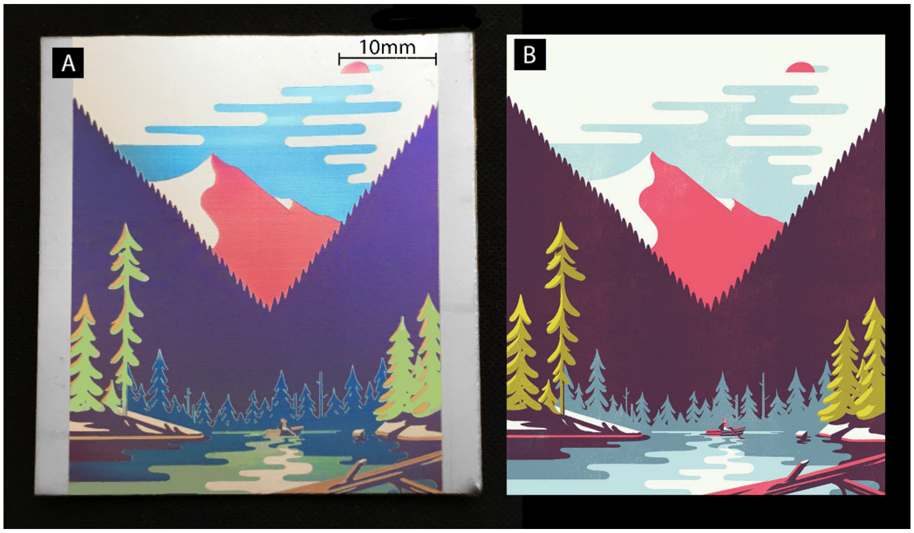

Fig. 3. Tom Haugomat's illustration for Air France magazine produced by laser radiation on the titanium surface (A) and the original picture, downloaded from https://www.behance.net/gallery/31744057/Air-France-magazine (B).

2.2 Metal coloration by laser production of silver nanoparticles

The coloring of the precious metals is also an interesting subject as they are widely used for creating masterworks in jewelry art. To make a jewel more colorful and attractive, we propose laser formation of metal nanoparticles on its surface. The color is achieved because of surface plasmon resonance of such nanostructures.

When high-intensive laser irradiation acts to the surface temperature overtakes the evaporation threshold generating metallic vapor. Due to convection in short time temperature rapidly decreases and the vapor condensation leads to spherical nanoparticles formation. These particles oxidize and partially precipitate back onto the surface, as presented in Fig. 4(a). Due to the surface plasmon resonance of produced nanoparticles, selective absorption of white light occurs, and the reflected wavelengths result in desired color formation, as illustrated in Fig. 4(b). The visible color depends on the size, shape, and distribution of produced nanoparticles. The novelty of this method includes using a nanosecond laser for nanoparticles formation.

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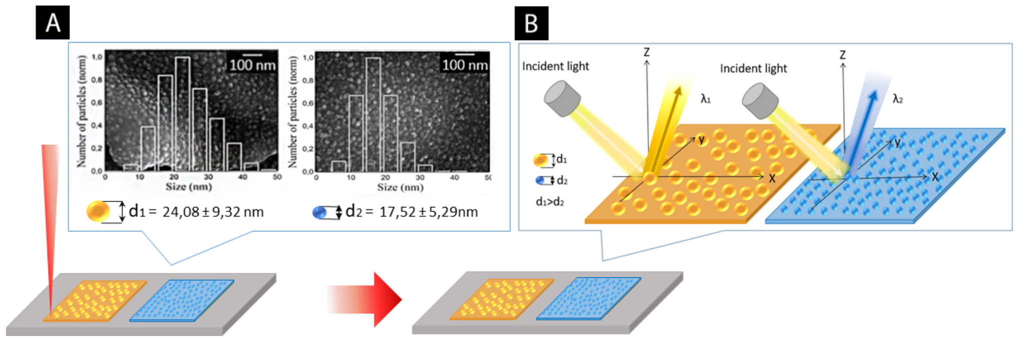

Fig. 4. Line-by-line color formation due to laser production of the silver nanoparticles: SEM images of the silver samples S3 and S1 and size distribution of nanoparticles (A); the process of the plasmon resonance in silver nanoparticles of a certain size (B).

Figure 5(b) shows the temperature range wherein a palette of colors on silver can be obtained and the Lab color coordinates of the samples. The spectral and colorimetric characteristics of samples are presented below. With the rise of the temperature the average size of NPs increases and the absorption peak redshifts, while NPs have a spherical shape. However, when the temperature reaches specific value (for silver is about 2500 K), NPs start to agglomerate and acquire non-spherical shape [21]. Indeed, the lowest light-blue spectrum in Fig. 5(a) (which corresponds to the sample S4) differs from others and is relatively plane due to NPs agglomeration. Moreover, it was observed that nanoparticles distribution also plays an essential role in the spectral characteristics of such samples. The smaller the average distance between particles the lower the wavelength of the absorption band.

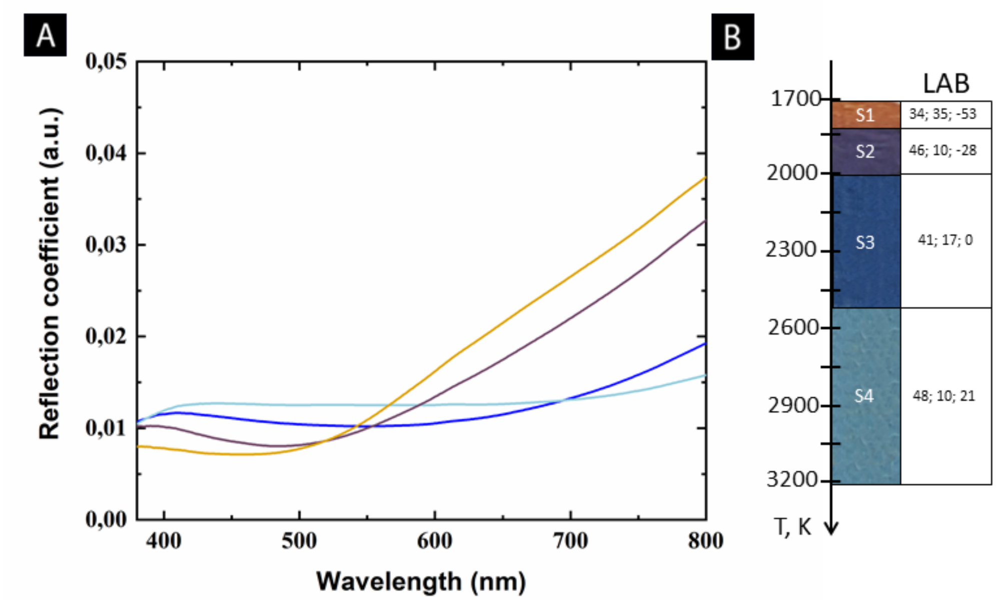

Fig. 5. Reflection spectra of the surface of silver samples after laser exposure (A), the temperature range for obtaining colors on silver (colors of reflectance spectra corresponds to LAB coordinates colors) and the Lab color coordinates of the samples (B).

Figure 6 shows silver jewelry colored with the usage of the palette above. Jewelry has been designed by "Procolorit" Ltd. to demonstrate the possibilities of silver surfaces coloration (see Visualization 1).

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Fig. 6. Examples of laser decoration of silver jewelry (see Visualization 1).

2.3 Metal coloration by laser structuring of the stainless steel surface

The technology of laser structuring of metals allows creating rainbow-colored images by forming periodic surface structures on metal. The mechanism of its formation is related to the presence of periodically modulated interference light field when irradiated with a laser. A possible way to obtain this modulation is an excitation of a surface electromagnetic wave. The formation of the periodical structure is possible by single-beam laser action [19,22,23].

Irregularities of the surface induce the dissipation of the light energy for each sequence of laser pulses. This provides the conditions to surface electromagnetic wave generation that starts to interfere with the initial laser irradiation creating nonhomogeneous temperature distribution. Such periodical distribution leads to resulting relief of the surface. The period Λ is consistent with the period of a surface electromagnetic wave rising along the surface: $\Lambda = \lambda / (n \pm \sin\theta)$ [24], where λ is the wavelength of the acting radiation, n is the refractive index, θ is the incidence angle of radiation.

In a typical case, when the laser irradiation acts perpendicular to the surface, the period of the structures is equal to the wavelength of the acting radiation considering n. For the polarized laser irradiation, it is easy to manipulate with the orientation of nanostructures which occur perpendicular to the polarization direction of the laser irradiation. These structures form a rainbow image consisting of elements that switch color depending on the viewing angle or angle of the illumination, as shown in Fig. 7(b). Also, it was experimentally found that laser-induced periodic surface structures formation occurs wherein the temperature range of 1210 K to 1670 K and is limited by the melting point of the material, which is presented in Fig. 7(a). Above the temperature diagram, microimages of the steel surface produced at different temperatures are demonstrated. It was observed that as the temperature increases, the surface melts and relatively thick oxide films appear. This oxide layer usually corresponds to tempering colors (what have been considered in section 2.1. for titanium) and here denies the possibility of periodic surface structures formation.

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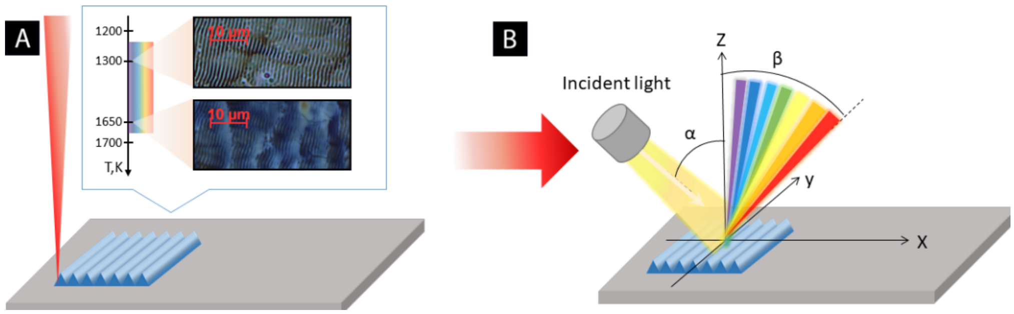

Fig. 7. Line-by-line color formation by laser-induced periodic surface structures (LIPSS) on steel: the temperature range for LIPSS and micro images of the steel surface treated at different temperatures (A), a plane wave incident on a periodic surface structure on the steel surface (B).

We improve our experimental setup to make possible changing the direction of polarization directly during the marking process. This enables creating dynamic effects as the smooth change of image color and movement of individual elements. This technology can be used both for coloring artworks with an unusual "holographic" effect and protection against replication by using the structured image as the unique signature. Laser-induced protective identification marks contain both visually observable and hidden features for authentication.

Figure 8(a) shows the visual features which include color change, color switching, and image streaming effects when observing or illumination from different angles. The hidden features include the presence of structures with the determined period and direction which can be seen under a microscope, which can be seen in Figs. 8(b) and 8(c), and the exact conformity of colorimetric coordinates with the calibration template developed in advance.

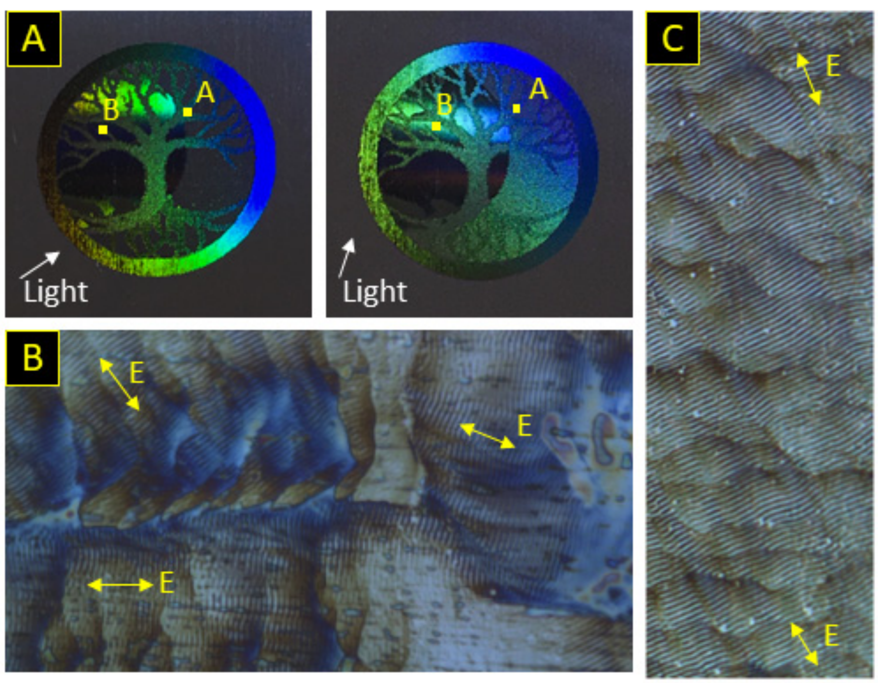

Fig. 8. Laser-induced images obtained on the structured surface of the steel. The effects of color change, color switching, and image streaming when observing or illumination from different angles (A). Micro images of laser treated areas with determined periodic structures directions (B) and with smooth direction change of the structures (C). Bilateral arrows indicate the direction of polarization of the laser radiation.

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3. Materials and methods

Cleaned with ethanol stainless steel AISI 304, commercial titanium Grade 2 and silver plates (0.925) with thicknesses of 0.7, 1 and 0.5 mm, correspondingly, were used for experiments.

Experiments were conducted in the air with the usage of a commercially available system based on ytterbium pulsed fiber laser with a wavelength λ = 1.06 µm, which produced nanosecond laser pulses of τ = 4-200 ns duration at repetition rates of f = 20–99 kHz. The focal spot diameter was 50 µm. Intensity kept in the range of $(1.2 – 50.9)\cdot10^7$ W/cm^2.

Samples before and after laser treatment were analyzed with Zeiss Merlin scanning electron microscope and Zeiss Axio Imager A1M optical microscope. To characterize the optical properties, reflection spectra within the wavelength range of 380–800 nm were recorded with a spectrophotometer SF-56 (LOMO)

The color coordinates were calculated according to CIE 1931 standard colorimetric methods (observer) for a 2° visual field, corresponding to the area of the highest clarity and chromaticity of the image perceived by the observer. Type C light source was used as a standard illuminant, representing average daylight with a low/partly cloudy sky which are ideal conditions for the observer.

4. Conclusions

In this article, we have demonstrated several novel approaches to Science Art based on laser technologies. We introduced three different methods that allow coloring different metals and apply various vibrant pictures and patterns with a very high resolution. On the one hand, these methods have different nature and result from different physical effects. In our work, we have described and analyzed thoughtfully each impact that leads to obtaining of colors in case of laser annealing (tempering colors), subwavelength nanoparticles formation (surface plasmon resonance) and structuring (diffraction on periodical structures). Deep understanding of described processes allowed us to summarize results and distinguish one universal parameter which can be used for controlling of colors in all the cases. Such characteristic is the operating temperature, which can be calculated for any material and parameters of laser processing.

Although the stability of color images was not under study in this work, it is evident that wear resistance of the obtained structures depends on the method of laser coloration. It was observed that the stability of colors obtained by NPs formation is not high enough due to the rapid oxidation of NPs in the air. However, such colors can receive this feature with the help of additional technological operations (for example, extra aluminum oxide cover) [16,25]. On the other hand, coloration by laser oxidation and laser structuring methods allows implementing rather stable color images which do not require special protection [26–29].

Moreover, all these techniques have high resolution and productivity (1.4 cm^2/min) of the image; they are green and contactless.

Therefore, here we multilaterally demonstrated that laser could be used not only as a highly useful industrial tool but also as a new exciting mean for Art and visual design.

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