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Laser coloration of titanium films: New development for jewelry and decoration

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ABSTRACT

In this work, we studied a technology of color images formation on a surface of titanium film deposited on silver and gold substrates. The coloration takes place due to film oxidation by the action of a fiber laser with nanosecond duration of pulses. Color coordinates for main colors obtained on gold and silver surfaces were calculated. According to measured reflectance spectra the final color resulted from both interference effects in the thin oxide film and substrate optical properties. Mechanical and chemical resistance tests of formed images demonstrated a high degree of adhesion between deposited titanium film and precious metals. Therefore, the proposed technology has a strong potential for jewelry industry implementation.

1. Introduction

The color image on a surface of jewelry is commonly used to make unusual and attractive items. Traditional techniques for coloration of precious metals are oxidation [1,2], hot and cool color enameling [3], electrolyte coatings [4] and others. Hot and cool color enameling uses additional layers negatively affecting on item lifetime. Color coatings made by oxidation and plating have been known for more than 35 years, but these processes do not allow high-resolution color images. Development of lasers made it possible to heat a metal surface locally and in a controlled way. Therefore, laser oxidation can be used to form a bitmap color image with a high resolution. To get an exact color one needs to control the temperature and an effective interaction duration [5], which are possible to regulate by changing the intensity I and the number of pulses per spot in a double-axis system N_x and N_y. Thermodynamic calculations [6] show that multilayer coatings of a complex composition are formed on the surface; this composition can be well correlated with experimental results [7–10]. The surface color originates because of interference effects in the upper oxide layer of a multicomponent film and the intrinsic color of the lower oxide film. However, the advantage of this method is based not only on a high level of laser radiation localization but also on the availability of a greater variety of colors for metals by optimizing the regimes [11]. For instance, the green color is possible to obtain for stainless steel, which is not feasible using other technologies.

Consequently, laser marking is one of the most state-of-art technological methods of recording color images onto the surface of metal products via its controllable laser oxidation [5,11–15]. One particular area of interest for this technique is jewelry. However, it is a known fact that precious metals are hard to oxidize in the air [16].

The method of laser coloring of precious metals under the influence of ultrashort laser pulses by using diffraction effects on the structured surface [17] was not applied in jewelry due to the high cost of such laser systems and the complexity of their implementation in the industry.

At the same time, color laser marking by fiber-optics lasers with a nanosecond pulse duration proved to be a technology allowing to record images with high resolution and excellent durability [18].

In this paper, a new method of using color laser marking in jewelry, based on the laser oxidation of the metal film deposited onto the surface of precious metal or a mineral is proposed.

2. Materials and methods

A silver substrate (.925 silver) and a gold substrate (.585 gold) were used as materials for the experiment. The dimensions of the silver plate were $20 \times 20 \times 0.5$ mm, of the gold one - $20 \times 10 \times 0.5$ mm.

The method of recording the color image onto the precious metal surface includes four stages of the processing of the original sample (Fig. 1).

The first stage consists of polishing the surface of the sample using Dialux Bleu compound. The polishing continues until the sample has a mirror shine ($R_a = 0.035$ μm).

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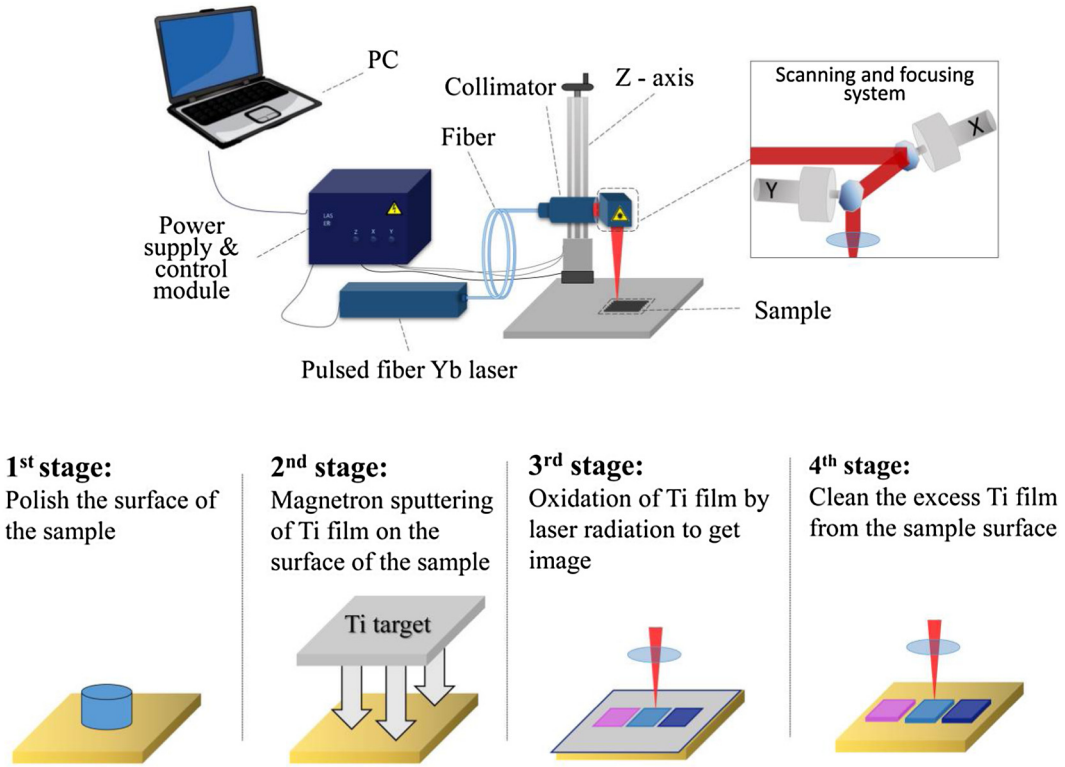

Fig. 1. The process of obtaining a color image on the surface of the piece of jewelry. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

The second stage is the sputtering of the metal film onto the piece of jewelry. In this work, Ti film with a thickness of 450 ± 50 nm is used. It is deposited using magnetron sputtering at the pressure of $2 \cdot 10^{-5}$ torr, the discharge current of 2 A, the discharge voltage of 385 V, sputtering time of 10 min and the target-wafer distance of 85 mm. Titanium was chosen because of the durability of the colored oxide structures formed on it.

The third stage of the sample processing is the programmed oxidation of Ti film via localized laser heating of the surface of the product. The laser exposure was carried out in air using a commercially available machine based on ytterbium pulsed fiber laser with a wavelength $\lambda = 1.06$ μm. The choice of the setup relies on the sufficient absorption of 1.06 μm radiation by metals and its serial production. The laser generates pulses of $\tau = 100$ ns duration at repetition rates in the range of $f = 20$–99 kHz with random polarization in a single pulse. The spot diameter in focus is $d_0 = 50$ μm. The oxidation of titanium was carried out via its heating in the air by a series of laser pulses with a line-by-line surface scanning at the speed V_{sc} in the range of 20–8000 mm/s. The number of pulses in the spot along the X and Y axis was calculated as $N_{x,y} = \frac{d_0 f}{V_{sc}}$. Laser intensity was $I = 10 \cdot 10^7$ W/cm^2, N_x lies in the range of 33–142, $N_y = 9$.

At the final stage, laser cleaning was done to remove excess Ti film from the surface of the product using the same setup. The cleaning took place under the following regimes of laser irradiation: $I = 2.55 \cdot 10^6$ W/cm^2, $N_x = 5$, $N_y = 9$.

Obtained samples were studied with the use of the optical microscopy (Zeiss Axio Imager A1M) and spectrophotometry (Ocean Optics CHEM4-VIS-NIR USB4000 with integrated tungsten halogen light source). PM-10 muffle furnace, ultrasonic bath and a rotary tool Dremel 4000, equipped with hard felt wheels (density of 0.70 g/c^3), were used for chemical and mechanical durability tests of the resulting colored oxide structures on the surface of the precious metals.

3. Results and discussion

3.1. Obtaining colored image on the surface of precious metals

Based on the analysis of previous results [5,11] one can see that the same surface color can be obtained by different laser processing regimes with the various combinations of I, N_x and N_y.

The color palette, achieved on the Ti film sputtered onto the surface of silver and gold can be seen in Fig. 2. For the brightest and the most distinct colors, the microimages of the surface are presented, from which it can be seen that the colored surface is non-homogeneous. It is caused by a non-homogeneous localized heating of the surface by a laser pulse with a normal distribution of intensity.

3.2. Spectral and color properties of the films

A reflectance spectra were measured on the experimental setup based on Ocean Optics CHEM4-VIS-NIR USB4000 spectrometer, halogen lamp light source, and two axes coordinate stage. Samples were being moved by an x–y stage with displacement field of 150 × 150 mm. The programmable microcontroller was used to control the stage. The light was delivered onto the surface of the sample via optical fiber. The lamp provided a defined shape of the spectral distribution of the radiation flux in the wavelength range of 360–2000 nm. The signal reflected from the target then entered the fiber probe that transferred it to the slit of the spectrophotometric system. This system generated a packet of measured data and transmitted it to PC. In turn, the spectrophotometer parameters were being controlled by PC and the resulting data were processed using specialized software.

Fig. 3 shows the reflectance spectra of the sample before and after laser processing. With an increase of N_x, the spectra appearance changes into a characteristic of light interference in a thin