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Laser Decoration of Precious Metals

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Abstract—A technique for the laser coloration of precious metals is described that is based on the oxidation of a titanium film deposited on the surface of a metal. When laser radiation acts on the film, it is heated and oxidizes. Depending on the radiation parameters, the resulting oxide films have different thicknesses and, due to light interference, they acquire different colors. The visible color of the surface depends on the angle of viewing after imaging. The aim of this work is to identify the color palette of a gold plate's surface with a thin film of titanium deposited on it. The titanium film is oxidized via fiber laser irradiation with a wavelength of 1.064 μm. Samples of color palettes are examined spectrophotometrically, and the chemical and mechanical stability of the resulting oxide coatings are tested.

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INTRODUCTION

Laser marking is one of the most cutting-edge technologies for applying color images to the surfaces of metal items via local laser oxidation [1–5]. The use of this technique in the jewelry industry is of great interest, but it is well known that virtually no precious metals oxidize in air.

Techniques such as oxidation [6], hot and cold colored enamels [7], and galvanic coatings [8] on are currently used to obtain color images on the surfaces of jewelry. However, they have a number of drawbacks, among which are the difficulty of producing detailed images, the fragility of coatings, and a limited color palette.

So far, the laser coloration of precious metals via diffraction on structured surfaces as a result of ultrashort laser pulses has not been widely used, due to the unreliability and high cost of such laser sources, and the difficulty of servicing them [9]. At the same time, color laser marking (CLM) using radiation from fiber lasers with nanosecond pulse duration has established itself as a technique that allows the application of images with high resolution and good wear resistance [10].

In this work, we propose a new technique of jewelry coloration based on the laser oxidation of a metal film deposited on the surface of a precious metal.

FORMULATION OF THE PROBLEM

The proposed CLM technique is based on the local laser oxidation of a metal by pulses of nanosecond duration as a result of line-by-line scanning of the metal's surface by a laser beam. Laser oxidation is determined by the temperature of heating for the area of the treated surface and the total time of exposure [11]. According to thermodynamic calculations confirmed by energy-dispersive and X-ray diffraction analysis, the pulsed laser heating of titanium in air produces a multilayered composite film on its surface. The lower layer of this film consists of Ti_2O_3 and TiO oxides with impurities of titanium nitride and titanium carbide, while the thin upper layer is transparent TiO_2 titanium oxide (IV) [12]. As a result, the surface color is determined by that of the lower oxides and the interference effects in the thin upper layer of the transparent oxide. An exception is gold tints, the mechanism behind the formation of which is determined by the golden-yellow color of titanium oxide (II), and not by interference effects.

EXPERIMENTAL

A polished gold plate 585° ($20 \times 10 \times 0.5$ mm^3) was used as the material for our experiment. The technique for producing a color image on the gold plate surface includes four steps (Fig. 1).

At the first stage, the gold plate is polished to a mirror shine ($R_a = 0.035$ μm) using a special polishing paste for jewelry and then degreased in acetone. At the second stage, a layer of titanium is deposited on the sample's surface; in this work, the sputtered film was 450 ± 50 nm thick. The titanium film is deposited on the surface of the precious metal via magnetron sputtering with the following parameters: pressure, 2×10^{-5} torr; discharge current, 2 A; discharge voltage, 385 V; sputtering time, 10 min; and distance to the substrate, 85 mm. Titanium was chosen as the metal

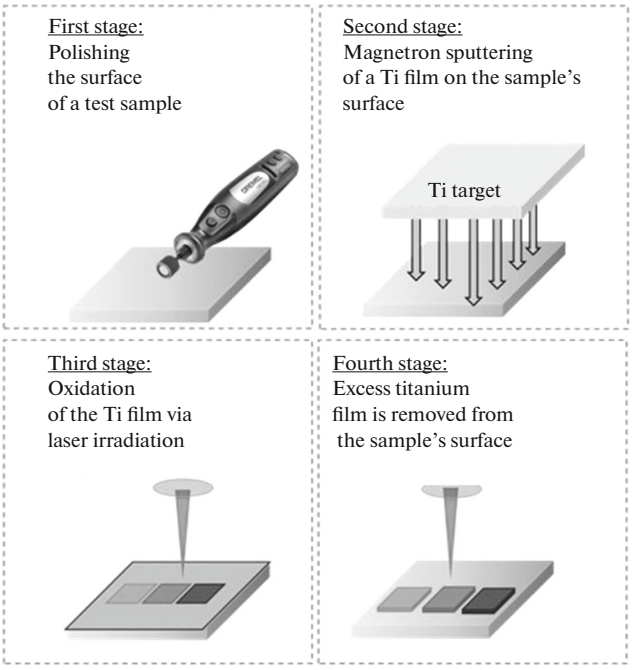

Fig. 1. Technique for producing a color image on surfaces of jewelry.

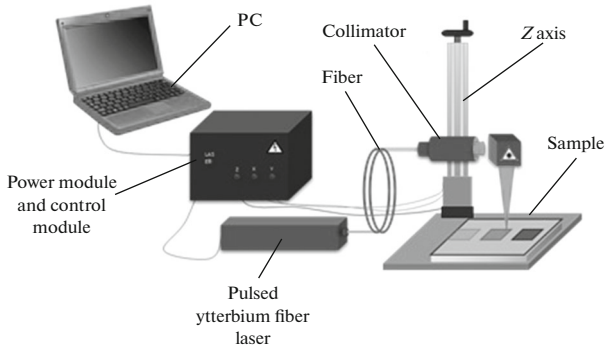

Fig. 2. Scheme of laser setup.

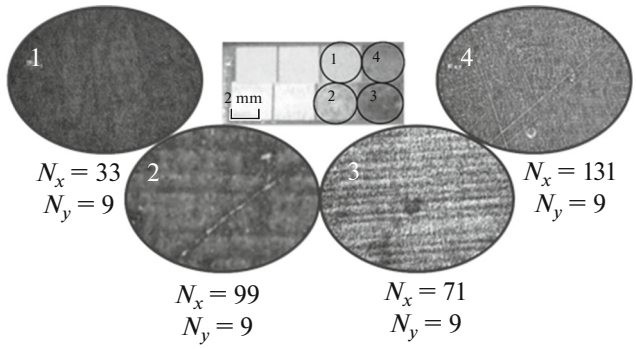

Fig. 3. Color palette and photomicrographs of samples 1–4 after laser irradiation.

for magnetron sputtering, since titanium dioxide has high stability of the resulting colored oxide structures to external influences [13].

The third stage of sample processing is oxidation of the titanium film by programmed local laser heating until a color image appears on the plate's surface. Laser irradiation was performed in air using a setup based on a Minimarker-2 pulsed ytterbium fiber laser (Fig. 2). The laser generates pulses with durations $\tau = 4–100$ ns at repetition frequency $f = 20–99$ kHz. The spot diameter at the focus is $d_0 = 50$ μm. To form oxide films with a specified thickness (color), radiation power density I is 7×10^7 W cm^{-2}, and the total number of pulses at the spot when scanning with overlap along the x and y axes is N_x (in the range of 33–142) and $N_y = 9$.

At the last stage, the excess titanium film on the jewelry's surface is removed by the laser on the same Minimarker-2 setup.

The optical properties of the samples were investigated via optical microscopy on a Zeiss A1M Axio Imager and by spectrophotometry. The reflection spectra of the obtained oxide coatings were measured on an Ocean Optics CHEM4-VIS-NIR USB4000 spectrophotometer, in which a halogen lamp was used as a light source, and a spectrophotometer equipped with a two-axis coordinate table.

To test the resulting colored oxide structures for chemical and mechanical stability on surfaces of precious metals, we used a muffle furnace, a Sapphire ultrasonic bath, and a Dremel 4000 drill with a polishing disc.

RESULTS AND DISCUSSION

Analysis of our experimental results and the literature data [1, 4] showed the same color of a surface can be obtained using different combinations of laser exposure parameters I, N_x, and N_y.

The color palette obtained on a titanium film deposited on a surface of gold is shown in Fig. 3. The surface color of the oxidized areas appears uniform when viewed with the naked eye, but from the microphotographs of we can see that the surface is in reality irregularly colored, due to uneven local heating of the surface.

To confirm the concept of how colored films form on a titanium film's surface, we measured the reflection spectra of a titanium oxide film on a gold surface (Fig. 4). A gold sample with a color palette was fixed on the coordinate table of the spectrophotometer and was moved relative to the measuring fiber (probe) along the X and Y axes. Reflection spectra with a specified scanning step in the range of 400–800 nm were measured within a field 150 × 150 mm in size, including the oxidized area. These spectra were used to calculate the CIELab values for each sample.

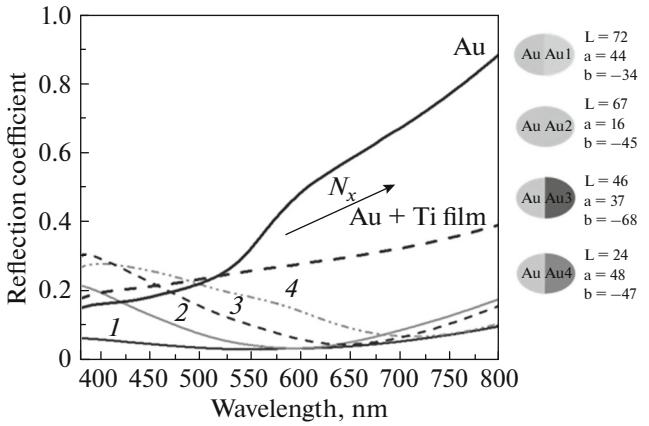

Fig. 4. Reflection spectra of a titanium oxide film on a gold surface.

It can be seen from the graph (Fig. 4) that as N_x grew, the reflection spectrum shifted to the IR region, as is characteristic of interference colors [1].

The reflection coefficient of gold with a titanium film (Au + Ti) in the wavelength range of 400–800 nm is less than that of uncoated gold (Au), so the final color of the surface is determined by interference effects in the titanium oxide film.

We were dealing here with titanium films 500 nm thick, but when applied to metal substrates, they should have had optical and thermophysical properties close to bulk titanium, and thus similar patterns of laser oxidation and color formation. This was confirmed in subsequent experiments.

It is well known that titanium oxide films exhibit elevated chemical stability, strength, and resistance to wear [13]. To analyze the stability of laser oxides, special experiments were performed on the environmental resistance of oxide coatings formed on the surfaces of precious metals under the action of a pulsed laser. Our tests for wear resistance were chosen such as to simulate the conditions of the use of jewelry in everyday life.

We performed the following tests for wear resistance, chemical and mechanical stability, and strength:

• abrasion with a cloth and a felt disk on a drill at a rotation speed of 6600 rpm for 5 min (test 1);

• chemical stability after holding in a 5% citric acid solution for 40 min (test 2);

• mechanical strength after holding in an ultrasonic bath with water for 20 min at temperatures of 20–60°C (test 3).

• thermal stability after hot soaking in a muffle furnace at 200°C for 1 h (test 4).

None of the above tests affected the visual or microscopic color of a surface (Figs. 5a, 5b).

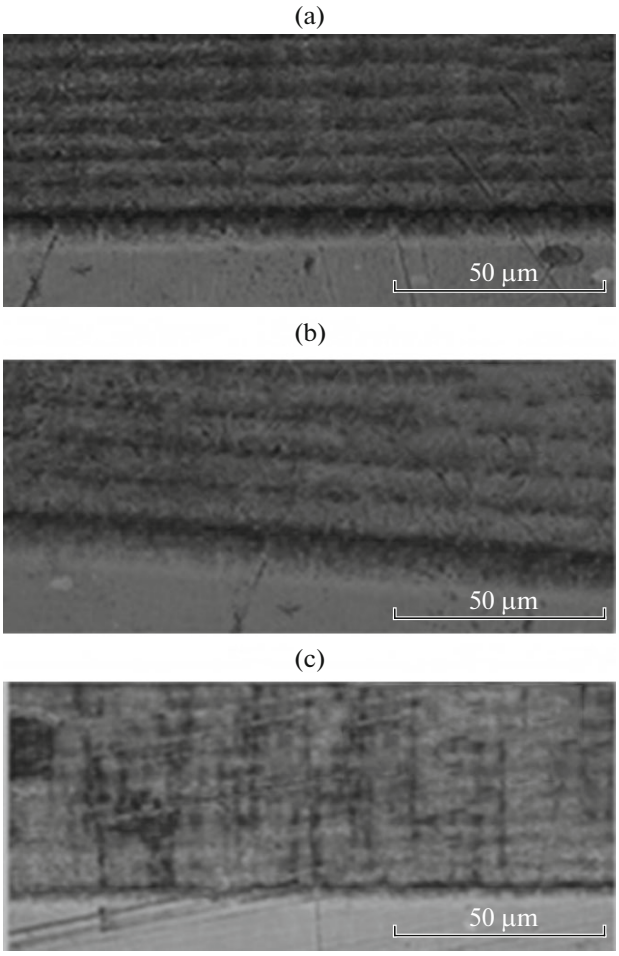

Fig. 5. Micrographs of an original sample (a) before tests, (b) after tests 1–4 (no visual changes), and (c) after scratching with a brass needle.

At the same time, scratching with a brass needle (Fig. 5c) did damage the coatings. The minor scratches acquired during tests are explained by gold itself being a soft metal with poor resistance to mechanical attacks.

CONCLUSIONS

A technique was described for producing color images on the surface of a titanium film deposited on a gold plate via its local oxidation by pulsed fiber laser radiation of nanosecond duration. It was confirmed that an image's color does not depend on the optical properties of the plate and is determined by interference effects in the oxide layer of titanium. In the future, other oxidizing metals could be used on surfaces of jewelry, expanding the potential palette of colors on surfaces of precious metal.

It was confirmed experimentally that our color oxide structures had high wear resistance to mechanical and chemical actions.

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