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Nanosecond pulsed laser irradiation of titanium: Oxide growth and effects on underlying metal

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Titanium oxide/oxynitride coatings were created on the polished surface of commercially pure, grade 2 titanium substrates by irradiating samples in air using a nanosecond-pulsed, infrared (1064 nm) fiber laser. Coatings consist of three distinct layers, including a thin TiO_2 rutile cap, a TiO middle layer, and an inhomogeneous bottom layer that is composed of TiO_xN_{1-x} and possibly oxygen-intercalated phases such as Ti_6O. The combined thickness of TiO_2 and TiO layers was varied from ~10 to 120 nm by increasing the accumulated laser fluence. Laser-grown coatings exhibit different colors, which vary with oxide thickness. The observed color is attributed to the interference of incident white light reflected from the upper and lower boundaries of the TiO_2 capping layer.

1. Introduction

Laser color marking is currently of interest for fabricating ownership tags, corporate or team logos, and decorative patterns on the exterior of valued assets and products [1,2]. Scanned laser processes show promise for tailoring intricate, color patterns that match specific designs, provided that the laser process parameters required to create a color on a particular material are known. In addition, laser color marking is being developed for producing random patterns for use as unique identifiers [3,4]. Unique identifiers are desired for protection against counterfeiting and related activities. As an example, a two-dimensional barcode identifier made on the surface of grade 2 Ti is shown in Fig. 1 to demonstrate the variety of colors made on this material.

Several methods of laser color marking have been reported in the literature. Traditionally, color marking has involved directing a focused or unfocused laser beam onto a metal or alloy substrate and heating the specimen to a temperature wherein one or more species initially contained within the solid react with a process gas to produce a transparent coating [5–9]. Oxide coatings can form during laser irradiation via photolytic and pyrolytic processes [10]. Research by several groups has demonstrated colored metal oxide coatings on different metals and alloys, including Ti [11–16] and stainless steel [17–19], and a large palette of colors is known to form on a few of these materials. The colored appearance of transparent oxide coatings is often attributed to the interference of reflected white light [11]. In addition, surface features such as plasmons and rough topography can give rise to color [20–22].

Despite its potential for fabricating identification tags, etc., the application of laser oxidization methods has been limited by a lack of reproducible, light-based processes. Early attempts to reliably mark a surface were confounded by unstable laser output. With the advent of modern lasers that offer precise and stable control of pulse energy, pulse duration, and repetition rate, there is renewed interest to improve upon prior work. The laser process parameters and the ambient environment affect the phase, microstructure, and thickness of coatings, and these properties can directly affect color. The optimization of the laser parameters is therefore critical to improving this traditional color marking approach.

Regarding pulsed laser color marking of titanium, recent work has investigated the structure and phase of produced coatings. Of note, Pérez del Pino et al. [11,14] show that a complex mixture of TiO_2, Ti_2O_3, TiO, and Ti_2O can form as a result of high power, nanosecond laser irradiation in air with oxygen-rich phases prevalent when using high laser fluences. This group further reports the thickness of oxide coatings to be in the range of 0.4 to 6 μm, although the authors clarify that the uncertainty of their measurements could be large [11]. Cross-sectional samples prepared by fracturing were imaged to reveal two layers having different grain structures [11], yet the phases associated with these layers were not distinguished. A variety of colors have been achieved on Ti substrates, and these are documented in several publications [1,11,14,23,24]. Nevertheless, a complete model that relates coating structure and surface morphology to optical appearance is still lacking.

Building on previous work, this paper investigates the detailed structure, phase, and composition of layers formed on Ti after nanosecond laser irradiation in air. The properties of coatings are probed after laser irradiation in order to develop a better understanding of how layered structure affects appearance. The cross-sectional samples of uniform

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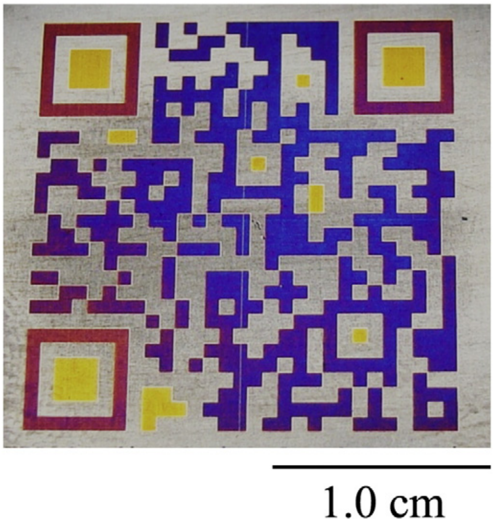

Fig. 1. Multicolor, two-dimensional bar code (QR type) created on titanium by scanned laser-stimulated oxidation. This pattern was created using an average power of 6.6 W, a repetition rate of 225 kHz, pulse duration = 119 ns and λ = 1064 nm. Colors were controlled by commanding laser scan speed as follows: blue (130 mm/s), red (180 mm/s), and yellow (240 mm/s). This 1-mm-thick demonstration piece was not used for testing.

thickness are prepared for transmission electron microscopy (TEM) and imaged using various methods to determine the phases formed and their location. In conjunction, high-resolution, energy-dispersive X-ray spectroscopy (EDX) is used to map the location of oxygen and nitrogen. These species diffuse into Ti as a result of laser heating, and the local changes in structure and composition are examined to distinguish the optically active parts of a coating. With knowledge of the layered structure that forms when using different laser process parameters, the palette of colors achieved by nanosecond laser-stimulated oxidation is explained in terms of transparent TiO_2 capping layers.

2. Experimental

Commercially pure, grade 2 (ASTM B265) titanium substrates were used for laser color marking experiments. All test samples were ground and polished using a Struers Abrapol-2 grinder/polisher to have final dimensions of 12.5 × 12.5 × 3.4 mm and a roughness (S_a) equal to 2–10 nm. Prior to laser marking, each test piece was cleaned by rinsing in Lenium™ degreasing solvent, followed by acetone and alcohol.

After cleaning, Ti samples were irradiated in air using an SPI laser pulsed fiber laser having a fundamental λ = 1064 nm. Laser marking involved irradiation at focus using a pulse frequency of 225 kHz and a pulse duration measured to be 119 ns. The beam exiting the fiber was collimated and directed through a variable beam expander onto two Nutfield steering mirrors. After reflecting off the steering mirrors, the beam was focused onto the surface of Ti using a Linos f163 f-theta lens. The beam was approximately Gaussian with a $1/e^2$ beam width equal to 59 μm at focus. A Dataray WinCamD camera and z-stage confirmed that the Rayleigh length was >1 mm, which is larger than the variation in working distance for leveled Ti samples. The relative humidity in the laboratory was ~30% during laser marking.

All color features created on test samples were 4 × 4 mm squares. Each color feature was created by scanning the focused laser beam over a specimen at constant speed and overlapping multiple, parallel lines. Upon the completion of a given line, the beam was blanked and then returned to the beginning of a neighboring, adjacent line offset by 10 μm. This offset, referred to as hatch, provides a substantial beam overlap of adjacent lines and a uniform fluence within a given feature. Results are discussed in terms of accumulated laser fluence. Accumulated fluence is generally expressed as

$$F_{\mathrm{acc}} = E_{\mathrm{p}}N_{\mathrm{p}}/A = P_{\mathrm{avg}}N_{\mathrm{p}}/Av \tag{1}$$

where E_p is the energy per pulse and N_p is the total number of pulses used to create a given feature of area A. Energy per pulse is expressed as average power (P_{avg}) divided by repetition rate (v). Accumulated fluences are specified in Fig. 2 for different scan speeds which determine N_p. A particular fluence can be accessed using either of the three powers (5.6, 6.6, or 7.6 W) selected for study by choosing an appropriate scan speed.

TEM, EDX, and X-ray diffraction (XRD) were used to evaluate oxide layer thickness, composition, and phase. Cross-sectional TEM/EDX samples were prepared in an FEI Co. Helios dual beam system using an *ex situ* FIB lift-out method [25]. FIB sections were aligned perpendicular to the direction of laser scanning in order to inspect across laser scan lines. Characterization involved an FEI Co. Titan G2 80-200 probe aberration-corrected transmission electron microscope operated at 200 kV. The system has an integral, 4-sensor, windowless, silicon drift X-ray detector array with a combined collection solid angle of 0.7 sr. The STEM detectors consist of a high-angle annular dark-field (HAADF) detector and three solid-state detectors (one bright field and two annular dark field). The microscope has a spatial resolution of 0.08 nm and high sensitivity to soft x-ray lines providing an ability to distinguish between species. The energy resolution of the EDX detector is specified by the original manufacturer to be 134 eV for Mn Kα. We have independently determined the energy resolution for this instrument to be in the range of 80–89 eV (full-width at half-maximum) for Ti L, N K, and O K lines. Chemical phases were identified by diffraction analysis and located using dark-field imaging methods. Phases formed by laser irradiation were confirmed using XRD. X-ray diffraction data were collected using a Bruker D8 diffractometer with a Hi-Star area detector. This system was configured with a sealed tube source (Cu Kα), an incident beam mirror optic (for removal of Cu Kβ radiation), and a 500-μm pinhole optic.

Scanning electron microscopy (SEM) was used to evaluate the extent of laser heating in Ti. Standard metallographic techniques were used to prepare large cross-sectional area samples for SEM. Sectioning involved cutting with an abrasive saw, encapsulation in cured epoxy, grinding to remove ~1 mm of material, polishing, and etching for 15 s in dilute hydrofluoric acid. As for TEM samples, SEM sections were aligned perpendicular to the direction of laser scanning. SEM involved a Zeiss Supra 55 VP electron microscope.

The spectral reflectance of oxide coatings was evaluated using a Varian Inc. Cary 5000 UV-Visible-IR spectrophotometer. Samples were

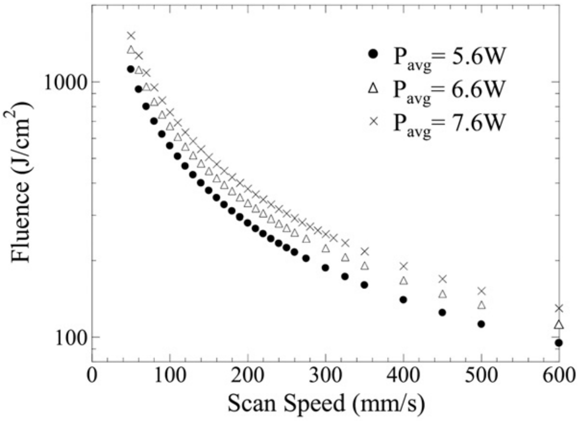

Fig. 2. Plot of accumulated fluences used for laser-stimulated oxidation of titanium substrates. Results are shown for the three different average powers and various scan speeds used for laser color marking.