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Nanosecond Pulsed Laser Color Marking of Titanium: Analysis of Oxide Layer Phase

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Abstract: Nanosecond-pulsed, infrared laser irradiation has been used to create metal oxide coatings on the surface of polished Ti for application as unique tags/identifiers. X-ray diffraction and electron microscopy demonstrate that coatings are titanium monoxide.
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1. Introduction

Laser color marking generally refers to techniques that create semi-transparent colored coatings by irradiation and subsequent surface chemical reactions. In the past, continuous wave and pulsed lasers have been used successfully to create a variety of distinguishable color coatings on the surface of metals [1,2]. Laser color marking is often described to be a pyrolytic process with heat generated within a substrate or a growing film stimulating chemisorption [3]. In other experiments involving high intensity pulsed lasers, photolytic processes contribute to oxide growth [4].

With this study, laser color marking of commercially available Ti is demonstrated and extended to the rapid fabrication of QR codes on metallic substrates. X-ray diffraction is used to evaluate the phases formed in color coatings in order to develop a better understanding of how the structure and the composition of laser-grown coatings affect colored appearance.

2. Experimental setup

A SPI Lasers, pulsed fiber laser was used to stimulate oxide growth on polished, commercially-pure grade 2 Ti. This infrared laser operates with λ = 1064 nm and has a maximum output power of 20 W. The beam exiting the fiber was collimated and directed through a variable beam expander on to Nutfield steering mirrors. After reflecting off the galvo-mirrors, the beam was focused on to a specimen using a Linos f163 f-theta lens. Pulse frequency (225 kHz), pulse duration (120 ns) and hatch (10 μm) were fixed for all experiments. Average power and scan speed were chosen to control feature color. All experiments were performed in air with a relative humidity level of ~15 %.

X-ray diffraction (XRD) data were collected using a Bruker D8 diffractometer with a Hi-Star area detector. The system was configured with a sealed tube source (CuKα), an incident beam mirror optic (for removal of CuKα radiation) and a 500 μm pinhole optic. Cross-section transmission electron microscopy (TEM) samples were prepared using an *ex-situ,* focused ion beam lift-out method and evaluated using a Tecnai F30-ST transmission electron microscope. Imaging and diffraction analysis were completed with the spatial resolution (pixel size) for TEM measurements ~8 nm. Composition was also evaluated using an EDAX super ultra-thin window energy-dispersive x-ray detector mounted on the transmission electron microscope.

3. Results and discussion

A variety of color layers have been made using average powers equal to 5.6, 6.6, 7.6 and 8.6 W. Feature color is controlled by changing the fluence and pulse overlap in a particular area. An example color pattern produced on the surface of Ti is shown in Figure 1. In this example, the color of isolated features is controlled by varying the scan speed with a fixed average power of 8.6 W. Each color pixel is 0.7 x 0.7 mm. Blue, yellow, orange and red features were obtainable and combined into a QR code pattern. Features have a diffuse reflectance when observed by eye.

Figure 1. Example color QR code created in the surface of Ti This Ti specimen was ~0.85 mm thick and 2.5 x 2.5 cm. This sample was irradiated in air, and it was not preheated before laser exposure. The color pixel size in this sample was 0.7 mm.

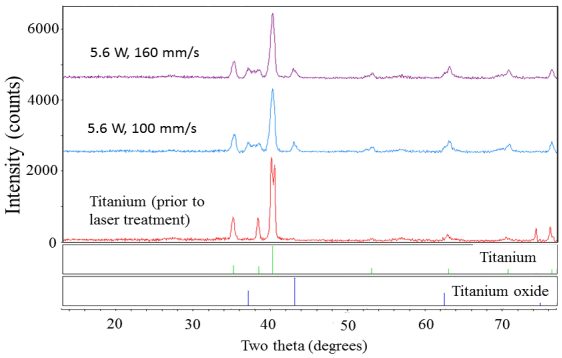

Figure 2. XRD patterns obtained from various oxide coatings made on the surface of commercially pure grade 2 titanium. The laser process parameters used to make these features are included above each spectra.

X-ray diffraction was utilized to determine the phases formed at the surface of laser-irradiated titanium. For phase characterization, oxide coatings were made uniformly over 4 x 4 mm areas using a fixed scan speed (and power). This area was sufficiently large for conducting X-ray microdiffraction studies of coatings. Figure 2 demonstrates that nanosecond pulsed irradiation in air creates titanium monoxide coatings (or TiO). Evidence for TiO is revealed by comparing the top two spectra shown in Figure 2 (obtained after laser irradiation) to the bottom spectra (taken prior to laser treatment). In particular, the reflections at two theta equal to 37.2, 43.2 and 62.6 degrees match the known reflections of titanium monoxide (TiO). Titanium is also detected when oxide coatings are present, consistent with a small oxide layer thickness. There is no evidence of TiO_2 or titanium nitride phases after nanosecond pulsed laser irradiation.

The oxide layers were analyzed further with TEM and energy dispersive spectroscopy (EDS). Selected area diffraction was consistent with the phase suggested by XRD, and EDS confirmed that coatings are composed of Ti and O. Further analysis showed the coatings are polycrystalline, and the presence of sub-surface defects indicates an extent of local laser heating to a few microns below the surface. The formation of hexagonal martensite (designated α') confirms local heating to temperatures in excess of the β transformation temperature (equal to 915 ^{o}C for grade 2 Ti) [5].

Optically-visible differences in color are likely the result of variations in the TiO coating thickness. Controlling the laser parameters will control the extent of localized laser heating and provide more control over oxide thickness, phase, and quality. Controlling these parameters will subsequently control both the optical and physical qualities of laser color markings rapidly produced on various substrates using ns laser irradiation.

4. Acknowledgements

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5. References

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