Applied Surface Science 387 (2016) 617–624

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Laser induced single spot oxidation of titanium

Tahseen Jwad*, Sunan Deng, Haider Butt, S. Dimov

School of Mechanical Engineering, University of Birmingham, Edgbaston, Birmingham B15 2TT, UK

ARTICLE INFO

Article history:
Received 25 May 2016
Received in revised form 21 June 2016
Accepted 23 June 2016
Available online 25 June 2016

Keywords:
Laser-induced colorizing
Titanium oxide
Single spot oxidation
Color patterning
Color coding

ABSTRACT

Titanium oxides have a wide range of applications in industry, and they can be formed on pure titanium using different methods. Laser-induced oxidation is one of the most reliable methods due to its controllability and selectivity. Colour marking is one of the main applications of the oxidation process. However, the colourizing process based on laser scanning strategies is limited by the relative large processing area in comparison to the beam size. Single spot oxidation of titanium substrates is proposed in this research in order to increase the resolution of the processed area and also to address the requirements of potential new applications. The method is applied to produce oxide films with different thicknesses and hence colours on titanium substrates. High resolution colour image is imprinted on a sheet of pure titanium by converting its pixels' colours into laser parameter settings. Optical and morphological periodic surface structures are also produced by an array of oxide spots and then analysed. Two colours have been coded into one field and the dependencies of the reflected colours on incident and azimuthal angles of the light are discussed. The findings are of interest to a range of application areas, as they can be used to imprint optical devices such as diffusers and Fresnel lenses on metallic surfaces as well as for colour marking.

1. Introduction

Titanium (Ti) oxides have received considerable attention by the research community and industry in the last two decades due to its attractive optical and surface properties [1,2]. In particular, its corrosion resistance, wear resistance, anti-galling properties, biological properties, high strength to weight ratio, good fatigue strength and aesthetic properties (permanent colours) [3], together with Ti mechanical properties [4] are very attractive for a wide range of applications, e.g. photocatalysis, gas sensing, medical implants, optical coatings [5], aerospace and parts identification [3].

Literature review shows that Ti oxide films can be generated by different methods such as heat treatment, immersion in hydrogen peroxide solutions, dipping in rutile and gelatine [6], passivation and anodizing [3]. Although some of these methods are similar and require an immersion of Ti samples into a chemical bath and then to apply DC power, the resulting thickness of the oxide films vary. Another important limitation is that the majority of these treatment methods are nonselective and the resulting oxide thickness is not totally controllable. In addition, high power and wet chemical bath are required, that make them hazardous processes [4].

It is therefore not surprising that oxidation of metals through laser processing is becoming attractive for applications requiring selectivity and high precision [7]. In particular, laser-induced oxidation can offer the following advantages over the other methods:

- Oxidation of pixels/spots with a resolution down to laser wavelength;
- High precision spatial-temporal control;
- Less processing time for relatively small processing areas;
- High repeatability.

Laser-induced colouring of metals can be achieved not only by creating thin films of oxide but also by generating laser-induced periodic surface structures (LIPSS). In particular, different colours were obtained on a range of materials by producing LIPSS employing lasers with pulse durations shorter than the electron-phonon relaxation time (one to tens of picoseconds [8]). LIPSS represents ripples that are usually perpendicular to the laser polarization and diffract light in different colours in the visible range depending on its incident angle. Such periodic surface structures find applications in optical coding [9] and image imprinting [10] and can be generated on a variety of materials such as metals [11–13] and semiconductors [14–16]. In this research only the laser-induced colouring of metals by forming a thin metal oxide layer with nanosecond pulse lasers is studied.

* Corresponding author.
E-mail address: taj355@bham.ac.uk (T. Jwad).

http://dx.doi.org/10.1016/j.apsusc.2016.06.136

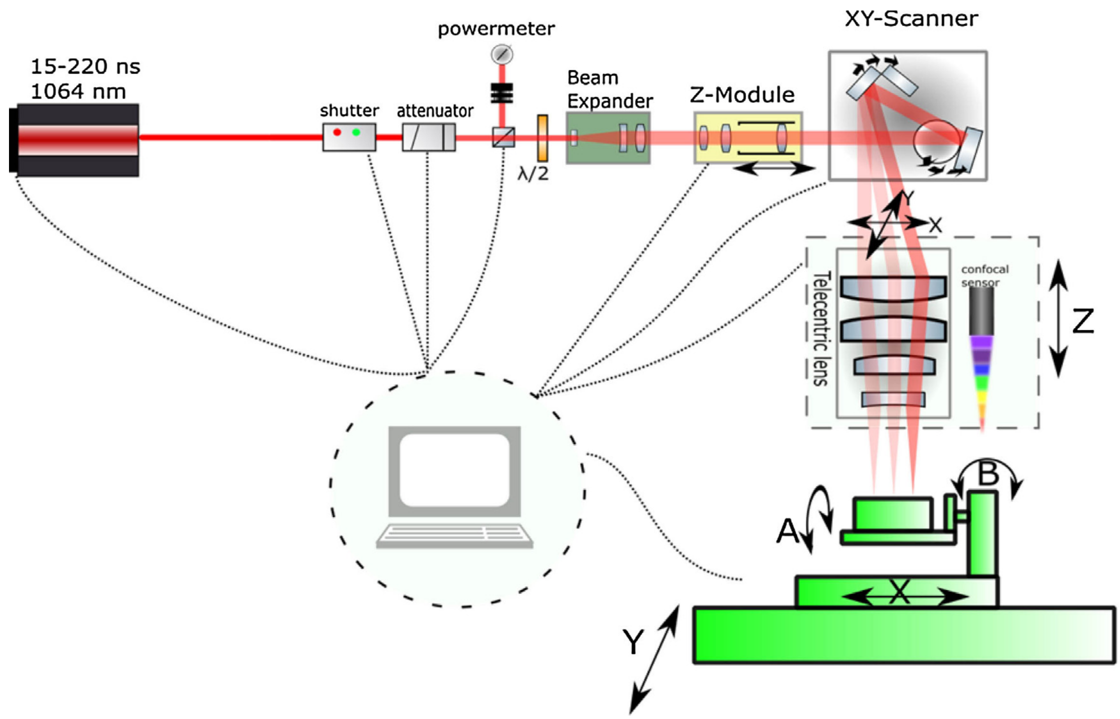

Fig. 1. Laser platform setup.

Laser-induced oxidation of different metals has been investigated by many research groups [17] in particular laser-induced colouring of Ti substrates, i.e. the composition and mechanism of laser-induced Ti oxides [5,18,19], the structures of Ti oxide films [2,7], laser-induced colouring versus anodizing [4], and the dependence of colours on laser processing parameters [1,19–21]. Applications of laser-induced oxidation of metals with its related colouring effects have been considered in jewellery and part identification [22–24]. However, the colourization process reported in the literature was carried out by laser scanning over a relatively large area as compared to the beam spot size. This has limited the applications of the process since the smallest fields of colours that can be produced are in millimetres scale. A comprehensive study of other potential applications has therefore not been carried out, apart from colour marking. The objective of this research is to develop a method to control the size of the oxidation area and its thickness on titanium substrates by laser-induced single spot oxidation and thus to imprint coloured image. By applying this approach the aim is to achieve a pixel resolution down to the beam spot size with high special control in the processed area.

2. Experimental setup

A nanosecond (redENERGY G4 50 W) laser from SPI Lasers is used in this research. With wavelength of 1064 nm and a 1 MHz maximum pulse repetition rate, it can be used for laser processing with 25 different pulse durations, from 15 to 220 ns. The beam delivery system used in this experimental study is shown in Fig. 1. The 3D scanner (RhoThor RTA) from Newson Engineering can realise scanning speeds of up to 2.5 m/s and the spot size can be controlled down to a few microns in the focal plane with the integrated beam expander and 100 mm telecentric focusing lens. The beam delivery setup is mounted on a mechanical z stage, while the workpiece is horizontally mounted on a high precision stack-up of four mechanical stages (two rotary and two linear Aerotech stages). The beam quality (M^2) is better than 1.3 and the output energy is controlled by an energy attenuator and monitored by an inline power meter. Commercially pure (Grade 1) titanium substrates with a 0.7 mm thickness were used in all the experiments in a temperature-controlled environment. Prior to laser processing, the samples were cleaned ultrasonically for 10 min in water and 10 min in acetone and dried with hot air. Alicona G5 Infinite Focus (IF) system is used to inspect the morphology of the processed Ti substrates, while the reflectivity measurements along the entire visible spectrum of wavelengths were performed using Ocean Optics USB2000+ Spectrometer with tungsten-filament lighting (CIE illuminant A) and Carl Zeiss Scope A1 optical microscope.

3. Single spot oxidation method

A single spot oxidation method is proposed in this research for a higher resolution than that achievable by applying raster scanning strategies. In addition, by applying this method different topographies can be created on the surface and thus the reflected colours to dependent on the incident and azimuthal angles. Thus, the objective is to achieve a higher resolution down to the beam spot size with high special control in the processed area together with an angular dependence of the colours due diffraction effects.

A single spot of oxide is created on the substrate by a pre-defined number of pulses (a pulse-train processing) that have fluence below the ablation threshold of Titanium. Then, the beam is re-positioned and the next pulse-train is delivered on the substrate and this is repeated until the area that has to be processed is fully covered. In this single spot oxidation method the colour coding is carried out by controlling the number of pulses and fluence, especially the cumulative fluence resulting from each pulse-train.

Initially, arrays of oxide fields were produced on a titanium substrate by applying the proposed single spot oxidation method. Each array included 10×10 square fields ($2 \times 2\,mm^2$ each) and each square contains (66 by 66) oxidation spots. For producing these arrays, the power is varied from 1% to 100% of the average power (50 W). The distances between any two successive spots in both X and Y directions were fixed at 30 μm while the beam spot size was 80 μm. Thus, the spots overlap. The pulse repetition rate was set to