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Abstract

Laser-induced oxidation of metallic surfaces such as titanium is used in many application areas for colour marking due to its selectivity, cleanness and processing speed. However, as the generated colours are permanent this reduces the flexibility and applicability of this laser processing technology. Therefore, a method is reported in this paper to erase selectively the oxide-based colours using laser-induced oxygen reduction. Especially, the colour marks are reprocessed in a low oxygen environment employing a nanosecond laser. A low fluence was used in order to diffuse oxygen out into the atmosphere and yield a lower form of metal oxides or a pure metal. Any cumulative fluence exceeding 25 J/cm^2 was sufficient to erase any laser-induced colours on titanium substrates. The XPS analysis revealed that all fields were mainly comprised of TiO_2 prior to erasing with only small contributions from Ti_2O_3 and TiO/TiN. Following the proposed laser-induced oxygen reduction, the relative concentration of TiO_2 decreased substantially while the overall amount of Ti in the near surface region increased. The results clearly show that the erasing of oxide-based colour marks is only due to oxygen diffusion back into the atmosphere and there were not any signs of laser ablation.

Keywords: nanosecond laser, Laser-induced reduction, metallization, titanium oxide, color erasing, color rewriting, color marking,

1. Introduction

Laser-induced oxidation of metals and semiconductors has gained a considerable attention by research community since it was reported for the first time in early 1970s [1]. One of the main advantages of laser-induced oxidation compared with other oxidation methods is the selectivity that differentiate and make this technology attractive for a range of applications [2, 3]. In particular, oxidation of titanium surfaces has many chemical, electrical, sensing, optical, tribological, and medical applications. This is due to the unique properties of titanium oxides compared to the substrate. One of the main applications of laser-induced oxidation of titanium is laser colour marking.

When pulsed (nanosecond or longer) or continuous wave (CW) lasers interact with a metal, a thin film of the metal oxides is formed due to melting and re-solidification of the substrate's material in air. The thickness of the generated film depends on used laser parameters, especially mainly on the accumulated fluence, and as result of the varying film thickness the surface can appear in different colours. This is due to the thin film interference phenomenon while the colours dependent on the oxide thickness.

Generally, the oxidation of titanium leads to a number of stable Ti-O phases such as Ti_2O, TiO, Ti_2O_3, Ti_3O_5, and TiO_2. However, TiO_2 (rutile) is the main structure and is the most stable side product of the oxidized Ti substrate [1]. The formed film consists of multilayers of oxides as stated by Del pino et al. [4-6], and others [7-10]. In addition, it was reported that the oxygen concentration is depth dependent, in particular, decreases with the depth increase [11, 12]. Two main layers constitute the film, i.e. the first is a transparent TiO_2 with some Ti_2O_3 on top that is followed by lower forms of titanium oxides, such as TiO and Ti_2O. The surface colourization is attributed to the transparent top layer that is due to the thin film interference

phenomenon mentioned above. At the same time, the underneath layer is opaque and has a metallic characteristics [6, 8], in particular its optical properties are very similar to those of pure titanium [13, 14].

Laser colour marking of titanium has been of interest to many industrial sectors, e.g. for aerospace, automotive, medical, optical and anti-counterfeit applications [15]. It is widely used to imprint product information, logos, and functional data on medical devices, implants, and surgical instruments [16, 17]. And, for this application area, it is critical the general surface properties of components, such as corrosion resistance and any performance characteristics [18, 19], to stay unaffected by the marking process. This is explicitly stated in ASTM F86 and F983 standards for permanent marking of implant components. In addition, the marking material should not be in anyway toxic. All these stringent requirements can be fulfilled by titanium dioxide that is the main side product on processed Ti substrates [1], i.e. it is nontoxic, biocompatible, and also exhibits negligible solubility in most solvents [20, 21].

Laser colour marking is one of the most flexible marking methods and this make the technology a very attractive proposition. However, as the generated colours are permanent this impacts its flexibility and applicability. Thus, capabilities to make such colour marks erasable and rewritable can broaden the application areas of this technology and can add one more advantage when compared with other methods.

Employing laser processing to remove paints (de-painting), oxides (de-oxidation), and rust (de-rusting) with different thicknesses was reported by Daurelio et al. [22], i.e. a very high fluence was applied to ablate paints and oxides. However, the oxides' removal in this case is performed by laser ablation and this leads to a range of negative side effects on the surfaces, e.g. changes in surface morphology and integrity, that affect the functional performance of

processed parts. In another research, Veiko et al. [23, 24] demonstrated the high mechanical and chemical wear resistance of titanium dioxides' thin films. In particular, neither the morphology nor the appearance were affected after treating the film by abrasion for 5 minutes, immersing it either in 5% citric acid for 40 minutes or in ultrasonic bath for 20 minute, and soaking it for one hour in 200°C muffle furnace.

Thus, colour surface marks induced on titanium surfaces by oxidation are very durable and cannot be erased by chemical treatments in various solutions [20, 21]. At the same time, any reprocessing of parts mechanically to remove such colour marks will affect their functionality and also will have cost implications. In addition, it is important to stress that neither chemical treatments nor mechanical processing can erase the Ti oxides selectively. Therefore, other methods for their selective removal should be sought.

In this paper, a method is presented for erasing colour marks on Ti substrates by laser processing in an oxygen controlled environment. In the next section, the methods and equipment used in the research are described and then the obtained results are presented and discussed. Finally, conclusions are made about the capabilities of the proposed method for metalizing transparent oxide layers and thus to achieve a metallic appearance.

2. Methods and equipment

In designing a method for removing colour marks in in the form of oxides on parts, it is important to take into account the specific requirements of various applications that can benefit from its implementation and also to have in-depth understanding of the laser-material interaction mechanism that should take place during the process. In particular, a method

should be designed for erasing colour marks, i.e. laser-induced oxides, on titanium surfaces that should be able to “reverse” the oxidation mechanism in creating them. Especially, when metals are heated in an oxygen rich environment, the oxygen reacts with their surface and free electrons are transferred from them into the adsorbed oxygen. As a result, ions are diffused through the native oxide layer to form thin oxide films [16, 25].

As it was stated above, the proposed erasing method should be able to reverse the oxidation process and thus to reduce/remove the oxygen from such oxide layers and as a result to yield a lower form of metal oxides or a pure metal. To achieve this the surface should be heated in a low oxygen environment, i.e. vacuum or inert gas, so that to diffuse the oxygen out into the atmosphere. Especially, the applied laser fluence should be less than the damage threshold, but at the same time sufficiently high to heat the oxides and thus to trigger the oxygen diffusion back into the atmosphere. Figure 1 illustrate the colorizing process and also the proposed method for erasing the laser-induced oxides.

Laser processing of materials in controlled environments have been used in different applications before. For example, it was applied to polish metal surfaces [26], nitride surfaces [27-30] and also to prevent the generation of oxides during laser cutting and texturing [31, 32]**.** In addition, laser processing in controlled environments was used to alter oxides’ conductivity, in particular through a laser induced reduction (also known as laser induced metallization) that involved a controlled laser heating in inert gas atmosphere. In this way, the properties of different oxides’ thin films were altered to become semiconductors, insulators or superconductors [33-37]. Thus, the proposed method should employ a similar laser-material interaction mechanism to perform so call laser-induced oxygen reduction.

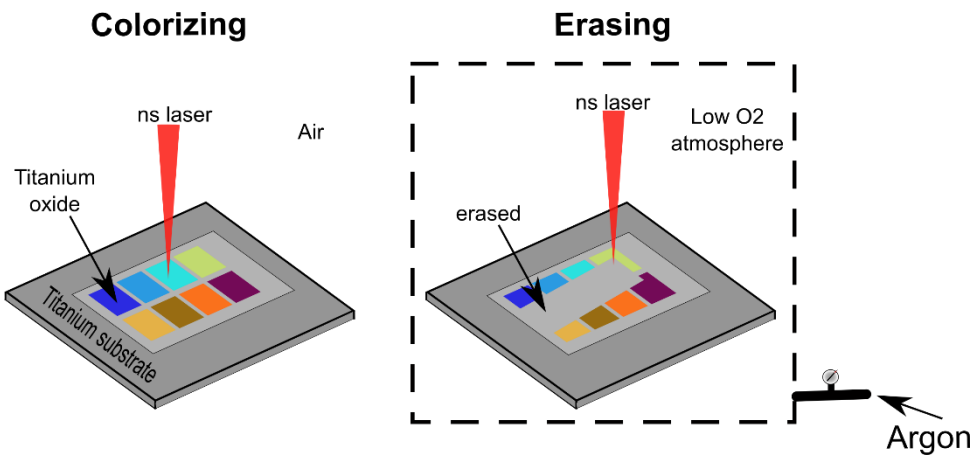

Fig.1. Schematic sketches of laser colour marking and erasing by laser-induced oxidation and laser-induced oxygen reduction, respectively.

An experimental study was carried out to investigate the proposed method employing a nanosecond fibre laser source (redENERGY G4 50W) from SPI Lasers. 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 experiments were performed on a reconfigurable laser micro processing platform with a 3D scanner (RhoThor RTA) from Newson Engineering and a 100 mm telecentric F-theta lens. The substrates were mounted horizontally on a high precision stack-up of mechanical stages from Aerotech. A specially designed chamber was employed to achieve a low oxygen atmosphere by purging the air and replace it with argon during the laser processing. The argon flow rate and the maintained pressure inside the chamber were 25 L/min and 5 Bar, respectively

The substrates used in the experiments were 0.7 mm thickness sheets of commercially available pure titanium (Grade 1). The samples were cleaned ultrasonically in water and acetone and then dried with hot air prior to laser processing. The morphology of the processed Ti substrates was inspected using an Alicona G5 Infinite Focus (IF) system.

Compositional analysis of the surfaces of several samples was carried out using x-ray photoelectron spectroscopy (XPS) measurements conducted on a Kratos Axis Ultra DLD spectrometer at the University of Warwick Photoemission Facility. The samples were mounted on to a standard sample bar using electrically conductive carbon tape and loaded in to the instrument. XPS measurements were performed in the main analysis chamber, with the sample being illuminated using a monochromated Al Kα x-ray source. The measurements were conducted at room temperature and at a take-off angle of 90° with respect to the surface parallel. The core level spectra were recorded using a pass energy of 20 eV (resolution approx. 0.4 eV), from an analysis area of 300 mm x 700 mm. The spectrometer work function and binding energy scale of the spectrometer were calibrated using the Fermi edge and 3d5/2 peak recorded from a polycrystalline Ag sample prior to the commencement of the experiments. The data were analysed in the CasaXPS package, using Shirley backgrounds and mixed Gaussian-Lorentzian (Voigt) lineshapes. For compositional analysis, the analyser transmission function has been determined using clean metallic foils to determine the detection efficiency across the full binding energy range.

As stated earlier, the colours obtained through laser induced oxidation are dependent on the oxide thickness. In particular, the main colours that can be produced on titanium surfaces by increasing the film thickness range from golden through orange, purple, blue, light blue to greenish blue. Thus, to validate the proposed erasing method, fields with increasing film thickness were created that represented different colour grades producible through laser-induced oxidation. In particular, the colours are generated by scanning the laser over the 10x10 mm^2 fields employing a zig-zag hatching strategy with a 20 µm hatch distance. The laser pulse repetition rate and pulse energy used were 1 MHz and 19.8 µJ, respectively that were selected based on the result in another experimental study [3]. The laser spot diameter

was 60 µm and thus an average fluence of 0.351 J/cm^2 per pulse was used in all experimental trials. The scanning speed was varied to process the fields and thus to produce TiO_2 with varying thickness and hence colours. Especially, the scanning speed was varied from 360 to 80 mm/s and thus to achieve a cumulative fluence from 58 to 260 J/cm^2 as stated in Table 1. The eight fields with varying colours on titanium substrates produced by laser-induced oxidation in air with these process settings as shown in Fig2. (a).

Table 1: laser parameters of fields number 1-8 in Fig2. (a).

Field number	1	2	3	4	5	6	7	8
colour								
Scanning speed (mm/s)	360	300	230	190	160	120	100	80
Cumulative fluence (J/cm^2)	58	70	91	110	131	175	210	260

3. Results and discussion

A set of experimental trials were perform to validate the proposed method for erasing colour marks through laser-induced oxygen reduction. Especially, TiO_2 fields on Ti substrates covering the whole range of colours in Table 1 were reprocessed in argon atmosphere with a varying cumulative fluence from 12 to 210 J/cm^2**.** The laser-induced oxygen reduction settings used in conducting these initial trials are given in Table S2. The efficiency of the reduction process is directly proportional to the irradiation intensity and inversely proportional to the oxygen concentration in the atmosphere [33]. Therefore, any processing of colours, TiO_2 fields, with cumulative fluence of less than 20 J/cm^2 leads to altering the colours' appearance but not to erasing them. At the same time, it was possible to erase all

colours with their corresponding TiO_2 film thicknesses with any cumulative fluence exceeding 25 J/cm^2 as shown in Table S2. The lowest cumulative fluence, i.e. 25 J/cm^2, was selected to investigate further the proposed method for erasing TiO_2 based colour marks in order to avoid any ablation and also to process the surface in the most efficient way.

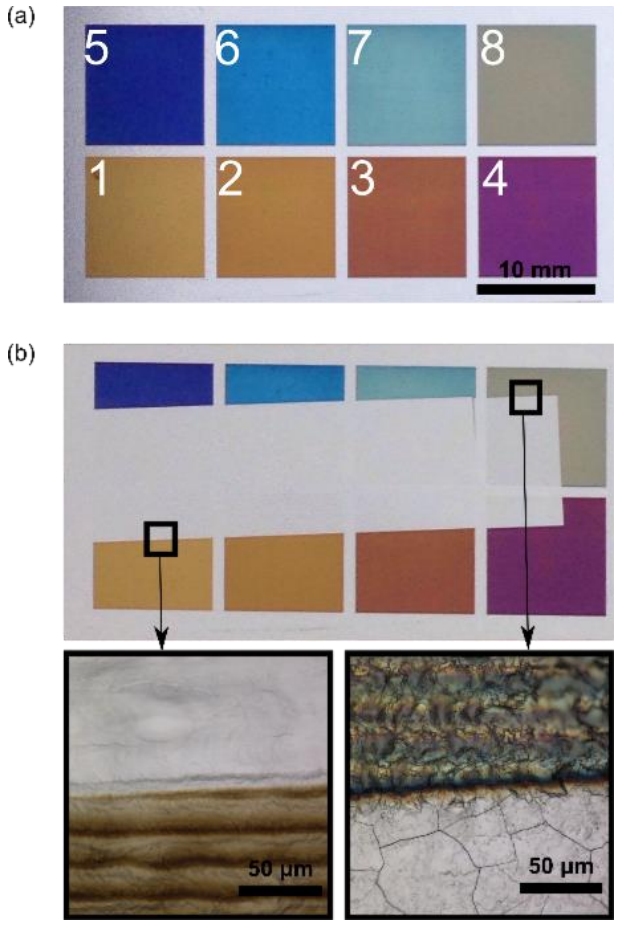

Fig.2. Eight fields of colours generated on titanium substrate. (a) before erasing, (b) after erasing.

Figure 2 shows the processed fields of colours before and after being erased using an accumulated fluence of 25 J/cm2. The roughness of the fields was almost the same before and after the erasing operation, in particular Sa of 0.5-0.6 um and 0.6-0.7 um, respectively, while

the Sa of the as-received substrate was 0.6 um. The cracks noticeable on the proceed fields, as shown in Figure 2, can be attributed to fast heating/cooling during laser processing. However, it is important to stress that they are formed during the colouring operation on the Ti substrates [38-40] and just become more pronounced after the erasing after erasing the TiO_2 film. There was no any traces of colours left on the processed area of the substrate and its appearance was similar to that of as-received Ti substrates.

To quantify colour differences between as-received substrate and the processed eight fields, the L*a*b* colour values were measured following the method in [3] and based on BS-ISO 11664-4-2011 and ASTM-D2244.16851. In particular, three measurements were taken for each of the eight processed fields and the average colour difference (ΔE_{avg}) and the maximum difference (ΔE_{max}) were 0.62 and 1.544, respectively. These quantitative assessment proves that there are no noticeable colour differences between the as-received substrate and the erased eight fields as ΔE_{max} is less than 2.3, the Just Noticeable Difference (JND) value [41].

The fields with the highest TiO_2 thickness, i.e. blue, light blue, greenish blue and yellowish blue, had some almost indistinguishable marks left after erasing them. These marks are colourless and they could be explained with the high surface roughness that results after laser-induced oxidation with high fluence. Also, these almost indistinguishable marks could be considered as an evidence that the TiO_2 erasing process is the result of deoxidation by oxygen reduction rather than ablation as the as-received substrate roughness is not changed. In addition, it is important to stress that the pulse's fluence used was 0.35 J/cm^2 and it was much less than the ablation threshold of titanium, in particular approximately 1.17 J/cm^2 for the same laser pulse duration and wavelength [42].

Fig.3. The three letters rewritten on the erased area of the colour marked fields

The objective of this research was not only to erase TiO_2 colour marks but also to develop a method that could be used to rewrite them on processed areas. Therefore, the acronym of the University (UOB) was rewritten over the erased area of the coloured field as shown in Figure 3. Especially, each of the letters in the acronym was produced with a different cumulative fluence, in particular 81, 120, and 220 J/cm^2, respectively.

The changes in the surface composition and film thicknesses were analysed employing XPS measurements prior to and after laser-induced oxygen reduction. Figure 4 depicts the Ti 2p spectra acquired from Field 3 in Fig. 2 (a) before and after erasing the colour, respectively. The significant differences in the surface composition are clearly seen in the figure.

The binding energy of the Ti $2p_{3/2}$ component for each specific compound were analysed further. Prior to erasing, the spectrum is dominated by the contribution from TiO_2 at 459.3 eV [43]. A small contribution at 457.0 eV was also detected that could be due to a very small amount of Ti_2O_3 in the near-surface region. No contributions from Ti(II) at 455.5 eV or metallic Ti at 454.0 eV were observed within the sampling depth of Field 3. A similar Ti 2*p* spectra was obtained for Fields 2 and 4 before applying the laser-induced oxygen reduction

(available in the supplementary information for the paper) and again the existence of a thick TiO_2 layer prior to erasing was detected on both fields.

After the erasing process (see Figure 4(b)), the Ti 2*p* spectrum revealed a reduction in the intensity of the TiO_2 components on all analysed fields along with increased contributions from multiple Ti oxidation states, namely TiO_2 (459.1 eV, 58.1 %), Ti_2O_3 (457.7 eV, 11.1 %), TiO/TiN (455.6 eV, 10.2 %) and metallic Ti (454.0 eV, 20.6 %). The metallic Ti 2*p* component was fitted using an asymmetric Lorentzian lineshape LA(1.2,5,8) that closely corresponds to the lineshape reported by Biesinger at al. [43]. Evidences of lower Ti oxidation states and metallic Ti in the spectrum suggests that the thickness of the TiO_2 film was reduced significantly and it was estimated to be approximately 2 nm after the erasing process (calculated using a thickogram [44]). Therefore, the erasing of the colours can be attributed fully to this significant reduction of the TiO_2 thickness after processing the area in Fig. 2 (b).

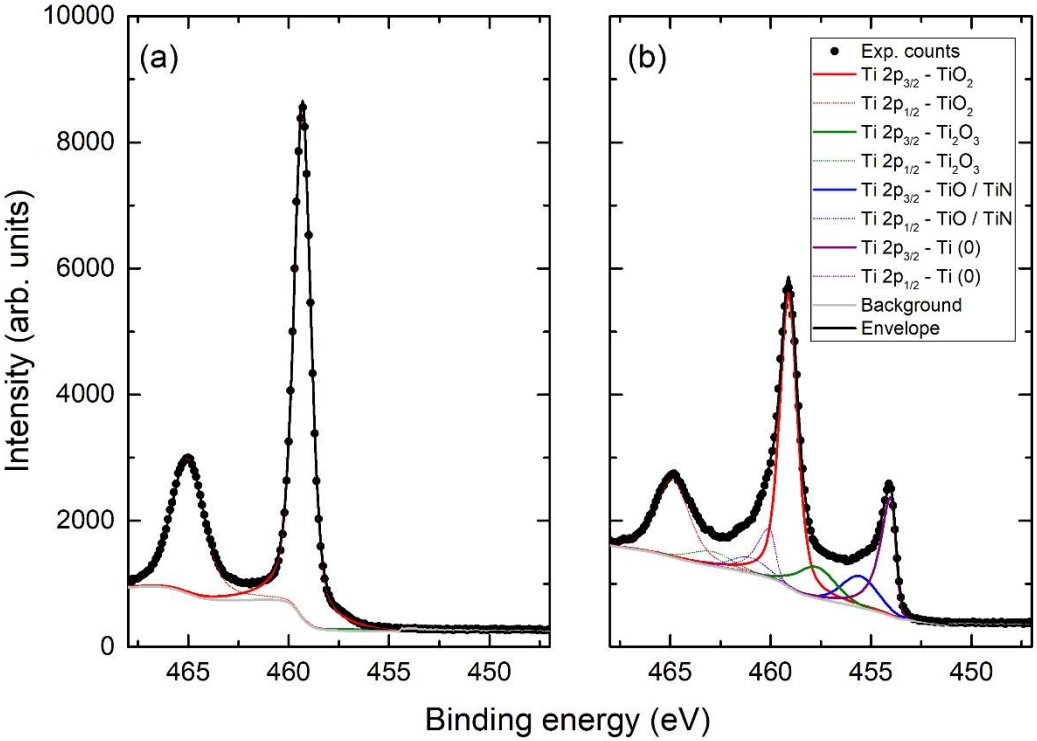

Fig. 4 Ti 2p XPS spectra obtained (a) before and (b) after the laser-induced oxygen reduction

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Further evidences about the TiO_2 layer thickness reduction was found in the O 1*s* spectra shown in Figure 5 that was obtained again before and after the erasing process from Field 3 (see Fig. 2 (a)). The total elemental compositions obtained for Fields 2, 3 and 4 compared with that obtained after the processing of Field 3 (referred to as 3prime) are provided in Table 2. The TiO_2 contribution to the total detected O 1*s* intensity fell from 79 % to 62 % and the Ti:O ratio increased from 0.42:1 to 0.53:1, both clearly pointing to a thinning of the TiO_2 layer such that Ti atoms in lower oxidation states are now within the sampling depth in Field 3.

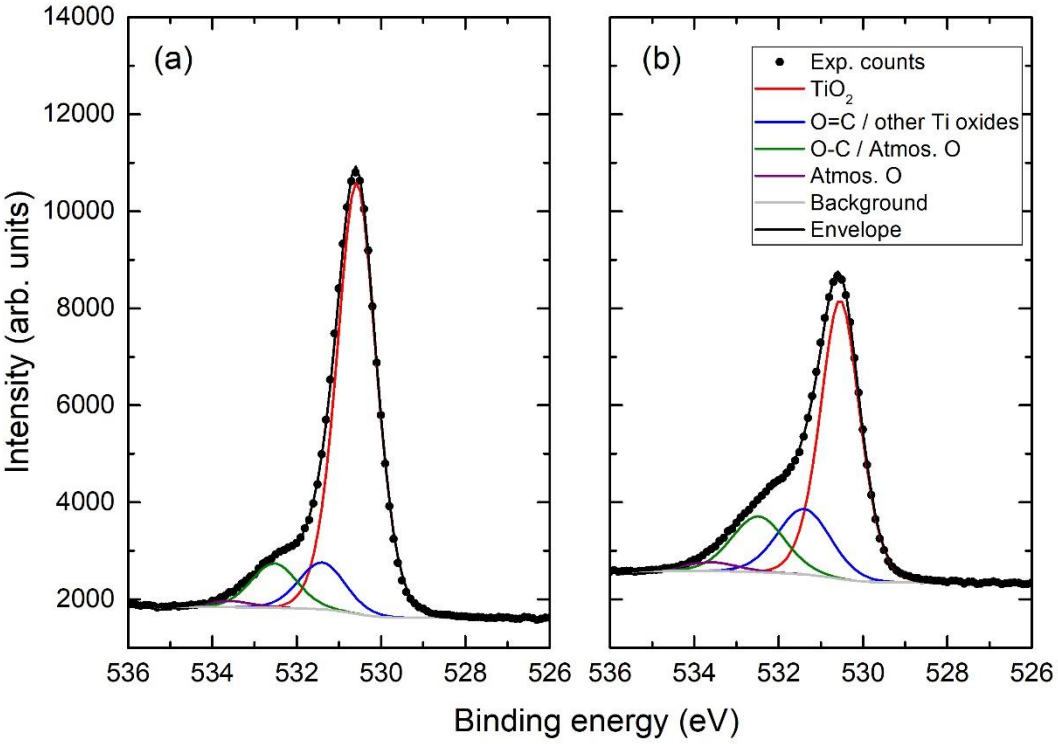

Fig. 5 O 1s XPS spectra obtained (a) before and (b) after the erasing process.

Table 2. Total elemental ratios derived from XPS measurements of Fields 2, 3, 4 and 3prime, accurate to +/- 2.0 %, together with the Ti:O ratio for them.

Sample	Ti	O	Ti:O	C	K	N	Zn	Ca	Na	Cl
2	15.8	39.6	0.4	40.1	0.3	1.6	0.7	0.7	1.2	0.2
3	18.1	43.5	0.42	35.6	0.2	1.5	0.3	0.4	0.5	0.0
4	16.6	40.9	0.41	35.3	1.4	1.2	0.3	0.5	2.9	1.0
3prime	20.3	38.6	0.53	37.5	0.0	3.3	0.1	0.1	0.1	0.0

The O 1*s* spectra obtained from Fields 2, 3, 4 and 3prime, available in the supplementary information for the paper, clearly demonstrate the presence of substantial TiO_2 layers on the

surfaces of all of three fields prior to the erasing process. The relative intensity of TiO_2 in the O 1*s* spectrum is significantly reduced for Field 3prime and thus the field exhibits a significant thinning of the TiO_2 layer. The associated C 1*s* and N 1*s* spectra for Filed 3prime are also provided in the supplementary information to the paper and they confirm the presence of a small amount of TiN (at 396.6 eV to 397 eV in the N 1*s* spectra) and the formation of a small amount of TiC during the erasing process (282.1 eV in the C 1*s* spectrum). In addition, the downward shift in binding energy of the C-C/C-H component in the C 1*s* region, from 285.8 eV in Field 3 to 285.5 eV in Field 3prime, points again towards a thinning of the TiO_2 layer during the erasing process.

It should be noted that in the Ti 2*p* region, the contribution from TiN overlaps with TiO at a binding energy of 455.5 eV to 456 eV, and also the contribution from TiC in Field 3prime was too small to be resolved. Correlating the various XPS spectra and the atomic ratios provided in Table 2, there is a noticeable increase in the relative amount of N in Field 3prime. This suggests either the formation of TiN in the near surface region during erasing, or some small inclusions of TiN below the surface in Field 3 that are revealed during the erasing process. Of the three fields before applying the laser-induced oxygen reduction, Field 2 exhibits the most TiN and sub-oxide species, suggesting that this field has a thinner TiO_2 layer compared to Fields 3 and 4.

4. Conclusions

A method is proposed for selective erasing of oxide-based colour marks by laser-induced oxygen reduction. The colour marks can be reprocessed with a low fluence with a nanosecond laser in low oxygen environment and thus to diffuse oxygen out into the atmosphere and yield a lower form of metal oxides or a pure metal. Eight fields with different TiO_2 thicknesses with their corresponding colours were selectively processed to erase laser-induced colour marks. Any cumulative fluence exceeding 25 J/cm^2 was sufficient to erase any laser-induced colours on the Ti substrates with only some almost indistinguishable marks left on fields with a higher TiO_2 thickness. These marks were colourless and were attributed to the high surface roughness that results after laser-induced oxidation with high fluence. The XPS analysis revealed that all fields were mainly comprised of TiO_2 prior to erasing with only small contributions from Ti_2O_3 and TiO/TiN. As a result of the proposed laser-induced oxygen reduction, the relative concentration of TiO_2 decreased substantially while and the overall amount of Ti in the near surface region increased. The results clearly show that the erasing of oxide-based colour marks is only due to oxygen diffusion back into the atmosphere and there were not any signs of laser ablation.

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