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Monitoring laser cleaning of titanium alloys by probe beam reflection and emission spectroscopy

D.J. Whitehead · P.L. Crouse · M.J.J. Schmidt · L. Li · M.W. Turner · A.J.E. Smith

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Abstract Studies have shown excimer laser cleaning to be an effective non-chemical alternative method for removing contaminants from surfaces of titanium alloys in preparation for electron beam welding and diffusion bonding, with reference to aerospace applications. Among several important criteria for process acceptability, is the absence of oxide formation. This paper investigates the viability of using a probe beam reflection (PBR) system and laser plume emission spectroscopy (PES) for detection of incipient oxide formation on three typical aerospace titanium alloys, viz. Ti64, Ti6246, and IMI834. These diagnostic techniques have been shown to be capable of sensing different components in the emission plume and yield quantitative results. Results from this work correlate closely with previously reported cleaning mechanisms. The oxidation threshold, as well as the operating window for successful decontamination, is discussed.

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D.J. Whitehead (✉) · P.L. Crouse · M.J.J. Schmidt · L. Li
Laser Processing Research Centre, School of Mechanical, Aerospace and Civil Engineering, University of Manchester, Sackville Street, Manchester, M60 1QD, UK
e-mail: David.Whitehead@manchester.ac.uk

M.W. Turner
Manufacturing Engineering Leader Compressors, Rolls-Royce plc., Inchinan Drive, Inchinan, Renfrewshire, PA4 9AF, UK

A.J.E. Smith
Rolls-Royce Compression Systems, Rolls Royce plc., P.O. Box 31, Nightingale Road, Derby, DE24 8BJ, UK

1 Introduction

Laser cleaning has been proven to be a credible alternative to the established chemical based processes with review articles on the subject available [1, 2] and numerous applications now industrialised, e.g. in artifact and art restoration [3], or the semiconductor industry [1]. A number of cleaning mechanisms are utilised, depending on the application. At relatively low irradiances (10^3–10^5 W/cm^2) and long pulse widths (micro to milli-seconds) or continuous-wave mode, selective evaporation can be employed. This requires the contaminant and substrate to have substantially different boiling points, and the ability of the substrate to withstand the heating cycle without degradation. In the short pulse-width regime (ns), higher intensity levels (10^7–10^{10} W/cm^2) are possible, resulting in plasma formation [4, 5]. The shock wave from the rapidly expanding plasma causes the removal of the surface-contaminant over-layers. However, there is a greater chance of damage to the underlying surface.

As shown previously, the most universally applicable laser cleaning technology for such aerospace components, delivering the most consistent and satisfactory results, has proved to be low-intensity short pulse excimer laser irradiation [6–8]. At low intensity using pulse widths of the order of 10 ns, the visco-elastic forces generated during the rapid heating and cooling cycles result in the generation of shock waves. These then facilitate the removal of contaminants without damage to the underlying surface. Excimer lasers offer considerable potential for applications in industrial environments due to their flexibility, consistency of operation, and high-automated productivity. However, in order to apply an excimer laser cleaning system in an industrialised process, it must avoid creation of undesirable side

Table 1 Composition of the titanium alloys

Titanium alloy	Composition
Ti64	90% Ti, 6% Al, 4% V
Ti6246	82% Ti, 6% Al, 2% Sn, 4% Zr, 6% Mo
IMI848	89.25% Ti, 5.8% Al, 3.4% Zr, 0.7% Nb, 0.5% Mo, 0.35% Si

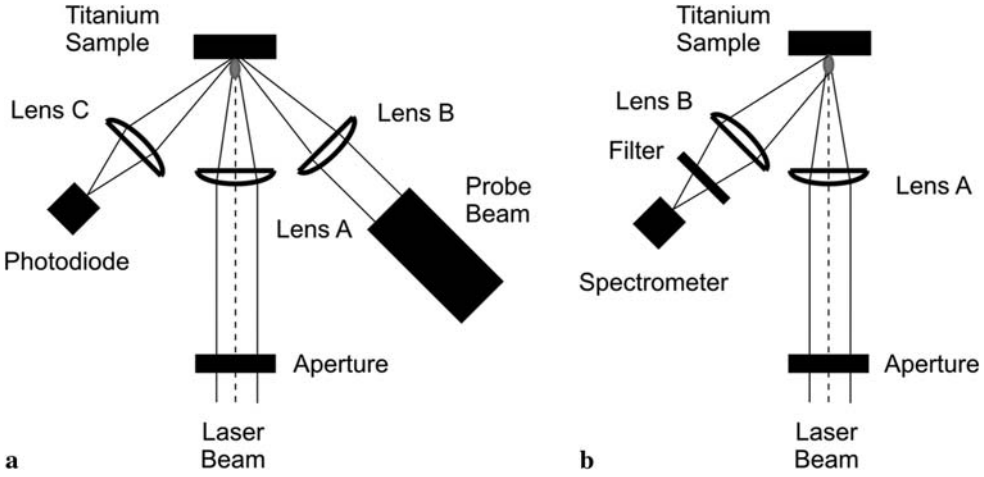

Fig. 1 Experimental setup (**a**) probe beam reflection (PBR) and (**b**) laser plume emission spectroscopy (PES)

effects, such as surface melting and surface reactions, (e.g. oxidation formation).

This paper extends previous work by the authors into laser cleaning by introducing probe beam reflection (PBR) [9–11] and laser plume emission spectroscopy (PES) [12, 13] to investigate the upper and lower fluence limits for laser cleaning and determine the operating window that can be used to avoid creation of undesirable effects. The test materials used were three typical titanium based aerospace alloys Ti64, Ti6246 and IMI848 (Table 1).

2 Experimental techniques

The experimental work was designed to determine the optimal cleaning conditions for irradiance of the targets without inducing any form of surface degradation of the alloys. Two experimental setups were used, as shown in Fig. 1a–b, utilising PBR and PES analyses. The laser cleaning experiments were performed using an industrial GSI Lumonics IPEX 848 pulsed excimer, operating using KrF ($\lambda = 248$ nm) with a maximum pulse energy of 500 mJ and pulse duration of 15 ns. Initial etch rate measurements were preformed to determine the upper fluence limit for laser cleaning using a simple optical projection set-up to give uniform laser fluence on the target. The rectangular output beam was passed through a small aperture to select a region of uniform fluence, and this area was then imaged onto the target using a spherical fused silica lens (lens A, focal length 150 mm). During the etch rate analysis the repetition rate was set to 1 Hz to avoid cumulative heating effects involved at higher rate. A range of different fluences was achieved by varying the discharge voltage of the laser system. The resulting etch depths were measured by characterisation of the craters using a Wyko NT1100 white light interferometer.

In-situ monitoring of the change in reflectivity was also undertaken during the etch rate analysis. A stabilised low power CW diode laser (ThorLabs LDM635) with a wavelength of 635 nm and a beam diameter of 3 mm has been employed in the probe beam system. This was focused by a BK7 lens (lens B, focal length 20 mm) approximately normal to the surface of each titanium alloy within the imaged excimer laser spot. The reflected light from the surface was then focused using a second BK7 lens (lens C, focal length 15 mm) into an Osram BPX65 photodiode in order to increase measurable intensity. The photodiode signal was recorded using a LeCroy Waverunner digital storage oscilloscope. The change in the intensity of the probe beam during the laser process was then monitored with each pulse.

For the emission spectroscopy, the probe beam and photodiode were replaced with an Ocean Optics HR4000 spectrometer (Fig. 1b). The irradiation process remained unchanged. As each laser pulse was incident on the sample, a bright emission occurred that extended a few millimetres from the surface. This region was imaged at 45° to the laser beam by a fused silica lens (lens D, focal length 100 mm) into an optical fiber, which in turn was coupled to the spectrometer. To eliminate scattered excimer radiation, a UV filter (<360 nm cut-off) was placed before the fiber. As previously, the change in the emission plume during the process was monitored with each pulse.

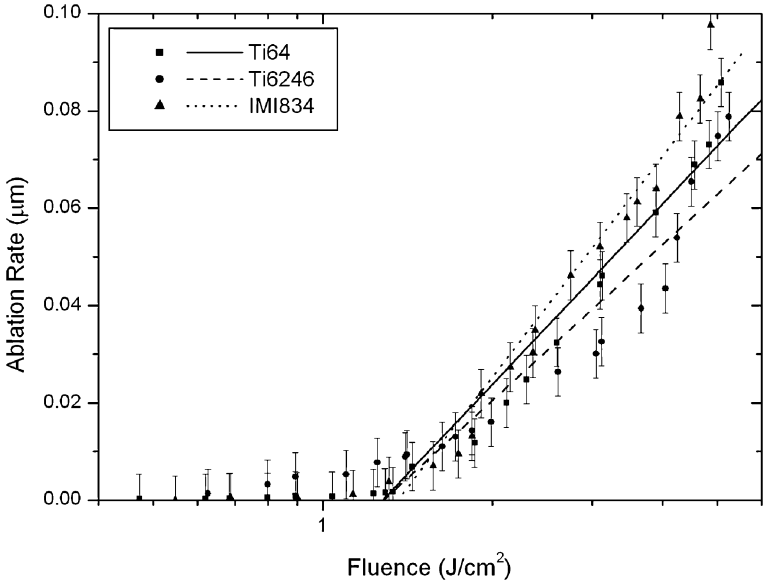

Fig. 2 Plot of ablation rate as a function of laser fluence for Ti64, Ti6428, and IMI848

3 Results and discussion

3.1 Ablation rate analysis

The upper process limits are determined by measuring the depth of an etch crater generated by exposure to a number of pulses (ablation rate). For each titanium alloy, the etch rate was found to be strongly dependent on the laser fluence as shown in Fig. 2. As expected, the threshold fluence F_T corresponds to the minimum fluence required for significant material removal. The dependence of the ablation rate x on the laser fluence F can be adequately expressed by Beer's law [5, 14] with α as an effective absorption coefficient:

$$x = \alpha^{-1} \ln(F/F_T). \quad (1)$$

Fits of the results in Fig. 2 to (1) found an F_T of 1.27, 1.28 and 1.35 J/cm^2 for Ti64, Ti6246 and IMI834, respectively. From the results it can be seen that for each alloy the received F_T is within a similar range despite a change in the alloy, and the results correspond to those previously observed [15]. As the fluence was dropped below the threshold, there was still evidence of small amounts of material removal occurring. This however is difficult to quantify. From the work previously carried out [8] it was determined that in order to clean the surface of the titanium alloys a fluence of approximately 0.5 J/cm^2 is required. Above this fluence, there is a high risk of degrading the alloy surface. The results, seen in Fig. 2, therefore, show good comparison to the previous work. The actual damage thresholds are substantially lower than the measured threshold fluence, since the first signs of surface damage are evidenced as oxidation, rather than melting, evaporation or ablation. Although these amounts of material are insignificant, they may still affect the criteria that determine whether the process is acceptable.

3.2 Probe beam reflection

During PBR, no changes to the material properties during the pulse were measured. Instead, the probe beam measured the change in the intensity of the reflected beam from the surface at a number of different fluences. In each case, there was a sharp initial rise in the reflected intensity of the diode laser occurring in the first few pulses, corresponding with the removal of any contaminants from the surface of the titanium (e.g. grease) [8]. When using the PBR experiment, it was found that at the threshold fluence and above, after the initial increase in intensity, the reflected intensity remained constant with the increase in the number of pulses. It is believed that this is caused by melt flow and material removal, which stop the formation of an oxide layer [16].

Below the threshold fluence at 0.52 J/cm^2, a decrease in the reflected intensity could be observed after approximately 50 pulses. Figure 3 shows examples of the signals obtained below the threshold fluence for each titanium alloy. The four graphs show a gradual decrease in the reflected intensity with the number of irradiating pulses. This gradual decrease continues until there is a sudden rapid drop in the reflectivity, corresponding with observations after the experiments identify an oxide layer on the surface.

From previous work when modelling the heat flow as a result of the laser interaction [2, 4, 16], the temperature rise and drop are very rapid, and the surface effectively returns to approximately room temperature before the start of the each successive pulse. While this temperature rise is above the oxidation threshold (~400 °C, [17]), this would suggest that there is insufficient time for an oxidation layer to form. However, with each additional pulse, there is a slight temperature rise of the bulk sample, and over a period of time (i.e. high number of pulses) this thermal accumulation on

the titanium can permit the formation of an oxide layer. This correlates with the high reaction enthalpy of oxidation of titanium as well as the fact that UV radiation has been shown to support the growth of oxide layers [18, 19].

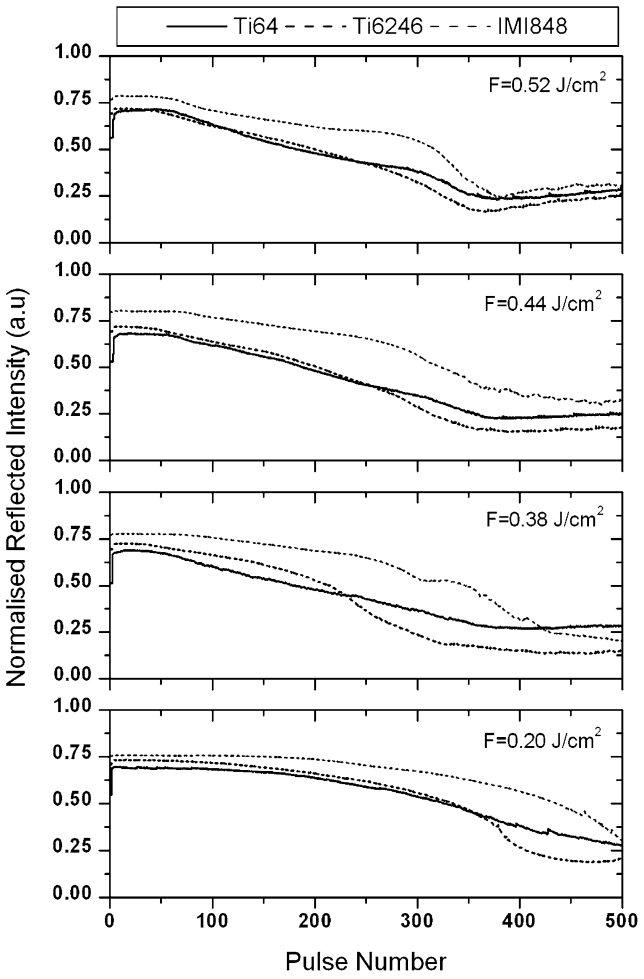

Fig. 3 Change in reflectivity with the number of pulses, at different laser fluences

3.3 Emission spectroscopy

Initial experiments found that in practise the emission spectra were almost identical for all alloy measured. Figure 4 shows a typical plume emission spectrum induced by laser irradiation of Ti64 at 0.7 J/cm^2. The emission lines corresponding to titanium and oxygen were identified from the established literature [20], small peaks of aluminium and vanadium were also discovered and are indicated in Fig. 4. Titanium neutral emission signatures represent the majority of observable peaks with the most intense emission at the spectral range from 498 to 502 nm. For oxygen, emission signatures included lines at 529.1, 547.7, 548.7, 551.1 and 625.9 nm. However due to their relatively low intensity, the titanium emission lines conceal these emissions within the spectrum.

It was found that as the fluence was decreased, the number of pulses required for these spectra to appear increased. The relationship between the number of pulses and fluence is shown in Fig. 5. Fits to the data gave the F_T of 1.10 J/cm^2, which compares well with the experimental data in Sect. 3.1 and also correlates with the drop in the reflectivity intensities shown in Fig. 3. These results suggest that the emission spectrum is a consequence of oxide layer on the surface of the target.

4 Conclusions

Experimental proof of the concept of excimer laser cleaning as a preparation technique for industry has been successful.

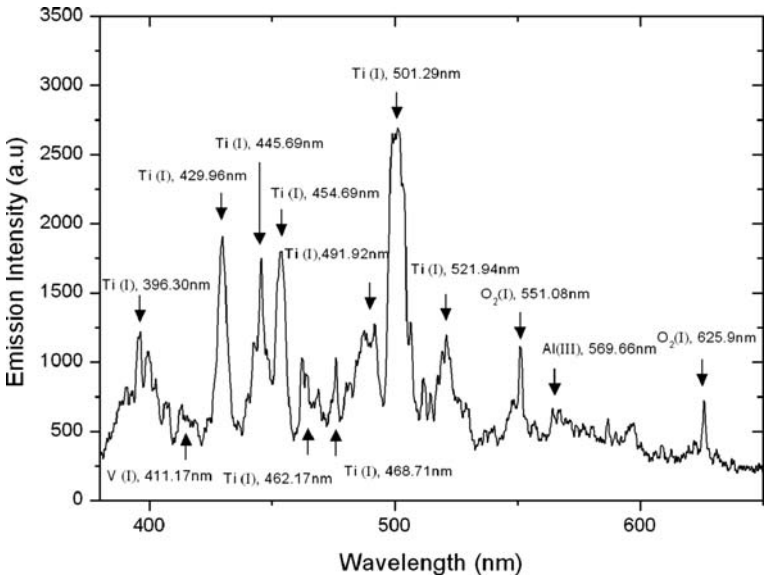

Fig. 4 Emission spectrum in atmosphere from Ti64 at 0.7 J/cm^2. The spectrum was recorded after 250 pulses

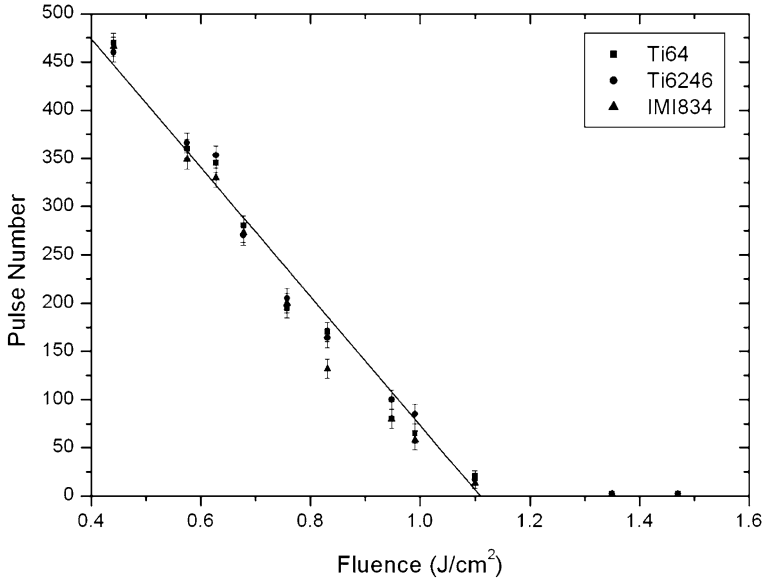

Fig. 5 Plot of the number of pulses required to generate an emission on the surface of Ti64, Ti6246 and IMI848 with respect to laser fluence

In order for a laser cleaning system to be applied as an industrialised process, it must avoid creation of undesirable side effects, such as surface melting and oxide formation. From the results presented successful laser cleaning of titanium surfaces can be best achieved between 0.3–0.5 J/cm^2 with 10–100 pulses needed to clean the surface depending on the laser fluence and the contaminants present on the surface. If the laser cleaning is attempted outside this window, either damage is caused to the surface, or the surface is exposed too many pulses so that an oxidation layer is formed. The effects of pulse repetition rate on the process can be significant, due to the resultant effects of the accumulation of thermal energy on the sample. However, this is beyond the scope of the work presented here.

The feasibility of PBR and PES as an in-situ analysis technique during an industrial cleaning process has been shown in principle, indicating the possibility of implementation in an industrial monitoring and process control system.

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