Comparative interaction mechanisms for different laser systems with selected materials on titanium alloys

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Abstract

This paper describes further research into, and modelling of, the interaction mechanisms of various laser types with materials, including synthetic oil and silicone grease. A Q-switched Nd:YAG pulsed laser, a CW CO2 laser, and a pulsed KrF excimer laser (λ = 248 nm) were used in the study. In general, the materials studied were very absorptive in the ultraviolet, less absorptive in the infrared, and least absorptive in the near-infrared. For the excimer, photo-ablation takes place, while for the other two wavelengths thermal vapourization dominates. In the case of silicone grease, full volatilization is only obtained using the excimer. For the other two wavelengths, this is not the case, with a sticky residue remaining after treatment. Interaction with synthetic oil with its lower boiling point can be obtained for all three laser types. With the Nd:YAG the dominant heating mechanism is conduction from the substrate and a baking effect is observed with strong interaction between the contaminant and the substrate. For the two pulsed lasers, oxidation is substantially less, while for the continuous wave CO2, the interaction time is sufficiently long for oxidation and secondary reactions to take place if care is not taken to work below the reaction threshold.

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1. Introduction

For laser systems to be credible candidates for the replacement for existing processes within a high-integrity engineering environment, an understanding of their mode of interaction with surface compounds and substrates is essential. Lasers offer considerable potential for application in production environments due to their flexibility, consistency of operation, high productivity when automated, and environmentally friendly credentials. This research has studied the interaction of different laser systems with a wide range of materials applied to titanium surfaces. Work previously reported by Turner et al. [1,2] described laser surface-processing systems based upon Nd:YAG pulsed and CW CO2 lasers. More recently, the programme has been extended to include the use of a pulsed KrF excimer laser (λ = 248 nm) for similar applications. This paper illustrates the relative effects by comparing the laser surface interactions of hydraulic oil and silicone grease, these compounds being two of the most tenacious chemicals investigated. Although, a range of titanium alloys has been assessed in the full programme, only Ti64 results are considered in this paper.

2. Experimental techniques

The first series of trials was performed on a Maxi Mark III Q-switched Nd:YAG laser, wavelength λ = 1064 nm, frequency range 1–30 kHz, spot diameter 180 μm, pulse length 100 ns, peak power 0.1–88 kW, and a focal length of 200 mm [2,3]. The beam incidence angle was maintained within 10° of the sample surface normal. The second phase of work was performed on a Spectron CO2 laser, λ = 10.6 μm, 130 W maximum power, operating in continuous wave mode, spot diameter 370 μm, and a focal length of 200 mm [1,3]. The beam incidence angle was maintained within 30° of the sample surface normal. The latest work was performed on a GSI Lumonics IPEX848 pulsed KrF excimer, λ = 248 nm, 1–100 Hz, pulse width 12–14 ns, 38 MW peak power, focal length 180 mm. The beam incidence angle...
was maintained within 30° of the sample surface normal. For each wavelength system, the substrate and surface compound absorption characteristics were assessed. Variations of laser fluence and traverse scanning speed were undertaken to determine the melt damage threshold conditions for the alloys. For the materials applied to the alloy surfaces, ablation thresholds were determined gravimetrically. Samples were processed in the as-supplied condition, and again with thresholds were determined experimentally and used in house by TGA–DTA, and remaining values taken from Clarson and Semlyen [10] and Incropera and DeWitt [6].

More extensive model calibration is part of the larger work programme. Apart from the ‘numerical calibration’ described above, a one-off calibration was done for the CO2 laser, using thermocouples in contact with the bottom surface of a 2 mm thick Ti64 plate. Comparison between experimental and predicted values can be seen in Fig. 1. Despite all the well-known errors inherent in 1D models [5], the results are close enough for the model to be considered useful, especially where exact measurements are experimentally untenable, such as during short-pulse cycles.

3.2. Treatment of laser interaction with surface contaminants

In this paper, we consider contaminants in the form of liquid films only. The beam couples directly with the contaminant, vapourizing and/or decomposing it by photolytic bond scission in the case of UV radiation. Extinction coefficients and fluence thresholds were determined experimentally and used in Eq. (1). The integration path was across the contaminant layer, with the volumetric source term calculated at each vertex from:

\[ Q(z, t) = \frac{I_0}{\delta_{BL}} e^{-z/\delta_{BL}} \]

and no equivalence of film and substrate interface temperatures assumed. In order to minimize numerical errors, the time and spatial increments were selected to yield equivalent results between the numerical solution for the surface temperature of the substrate metal, without a contaminant film and below phase transition, and the analytical solution of Eq. (1), formulated in terms of temperature only, found in e.g. Steen [5]. Verified Ti64 physical properties were used [9]. Specific heat values for the applied compounds were determined in house by TGA–DTA, and remaining values taken from Clarson and Semlyen [10] and Incropera and DeWitt [6].

3. Thermal model

3.1. Base model

A one-dimensional finite difference thermal model was developed in parallel with the experimental work for a first-order evaluation of temperature histories and for postulating laser-interaction mechanisms. Time-dependent temperature distributions were calculated explicitly from a central-difference discretized formulation [4] of Fourier’s second law, i.e. from:

\[ \frac{\partial H}{\partial t} = k \frac{\partial^2 T}{\partial z^2} + Q(z, t), \]

where \( H \) is enthalpy, \( T \) the temperature, \( z \) the depth, \( k \) the thermal conductivity, \( \rho \) the density, \( t \) the time and \( Q(z, t) \) is a power source term [5,6]. This is the more convenient form when addressing phase change [7,8], and is in line with the derivation of the equation. The boundary and initial conditions used were:

\[ z = 0 \text{ (substrate only), } I_0 = \frac{P(1 - R)}{A} = -k \frac{dT}{dz}; \]  
\[ z = L, \quad \frac{dT}{dz} = 0; \]
\[ t = 0, \quad T = 298 \]

where \( I_0 \) is irradiance, \( P \) the input laser power, \( A \) the beam area, \( R \) the reflectivity, and \( L \) is the thickness of the substrate. At the interface the thermal conductivity was estimated from:

\[ k_{\text{combined}} = \frac{k_{\text{film}} k_{\text{alloy}}}{k_{\text{film}} + k_{\text{alloy}}} \]

and no equivalence of film and substrate interface temperatures assumed. In order to minimize numerical errors, the time and spatial increments were selected to yield equivalent results between the numerical solution for the surface temperature of the substrate metal, without a contaminant film and below phase transition, and the analytical solution of Eq. (1), formulated in terms of temperature only, found in e.g. Steen [5].
3.3. Oxidation kinetics

Many papers addressing the kinetics of oxidation of titanium surfaces have been published, e.g. [11–15], but very few are available for Ti46 and other titanium alloys. In-house data [16] were used for evaluation of oxide formation. A parabolic law assumed to apply throughout the temperature range, and oxide layer thickness $z$ is calculated from:

$$z^2 = k_{R,n} \cdot t$$

(7)

after a surface temperature history had been computed. Here $k$ is the temperature-dependent rate constant determined to be:

$$k_{R,n} = 2.6858 \times 10^{11} e^{-(199168/RT)} \mu g^2 \ cm^{-4} \ s^{-1}$$

(8)

with $R$ the ideal gas constant.

4. Results and discussion

4.1. Damage thresholds

The experimental melt damage thresholds for pre-etched Ti64 were found to be $1.6 \times 10^6$, 708, and 450 mJ cm$^{-2}$ for CO$_2$, Nd:YAG, and excimer wavelengths, respectively. Reverse calculations give reflectivity values of 92, 73, and 75% at these wavelength. This is in line with values for metals quoted by e.g. von Allmen and Blatter [8]. The conditions at which the melt damage thresholds were determined were: a full interaction time of 14.8 ms for the CO$_2$ laser, a 90-pulse train at 25 kHz for the Nd:YAG, and a 10-pulse train at 100 Hz for the excimer.

Specific mass removal rates as function of fluence for the excimer are given in Fig. 2, for synthetic oils and silicone grease. From this it is clear that ablation depth is not a linear function of the logarithm of the fluence. The pulse fluence selected for reaction with the applied material was selected at a convenient position between the threshold fluence and the damage threshold for the substrate, typically 150–200 mJ cm$^{-2}$ for the excimer, and 400–500 mJ cm$^{-2}$ for the Nd:YAG.

4.2. Oxidation rates

The temperature history for the substrate surface and concomitant predicted oxide film thickness during typical operating conditions are given in Fig. 3, for the three laser systems. These predicted values are in line with preliminary experimental observations and surface analysis data. In the case of the excimer, the post-treatment surface displays increased reflectivity without any sign of discoloration. Despite the fact that the maximum temperature is above the oxidation threshold ($\approx 400 \ ^\circ C$ [9]), the temperature rise and drop are very rapid and the surface effectively returns to room temperature before the start of the each successive pulse. There appears simply insufficient time for oxidation, which is diffusion controlled, to occur to any significant degree. The maximum temperature predicted for the Nd:YAG case is higher and approaches the $\beta$-transus of the alloy, and there is a slow build up of residual temperature between pulses. This base temperature remains under the oxidation threshold and oxide growth takes place only during the high-temperature sweeps. Again the time scale is such that oxide growth is minimal, and a few nm only are predicted. In the CO$_2$ case, the surface remains above the oxidation threshold for tens of ms, and oxide films of some 200 nm area predicted. This agrees with our qualitative experimental observations and XPS results below, that obvious discoloration typical of interference effects are observed.

4.3. Laser interaction mechanism

The Beer–Lambert penetration depths and fluence thresholds given in Table 1, only the low fluence values were used in linear fits of ablation depth as function of the logarithm of the fluence. The pulse fluence selected for reaction with the applied material was selected at a convenient position between the threshold fluence and the damage threshold for the substrate, typically 150–200 mJ cm$^{-2}$ for the excimer, and 400–500 mJ cm$^{-2}$ for the Nd:YAG.

![Fig. 2. Excimer material ablation rates.](image)

**Table 1**

<table>
<thead>
<tr>
<th>Material interaction properties</th>
<th>$\lambda$ ((\mu m))</th>
<th>$\delta_{BL}$ ((\mu m))</th>
<th>$F_{Threshold}$ (mJ cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Synthetic oil</td>
<td>10.6</td>
<td>390</td>
<td>350</td>
</tr>
<tr>
<td>Silicone grease</td>
<td>10.6</td>
<td>2</td>
<td>-</td>
</tr>
<tr>
<td>Synthetic oil</td>
<td>1.06</td>
<td>$\infty$</td>
<td>-</td>
</tr>
<tr>
<td>Silicone grease</td>
<td>1.06</td>
<td>10,500</td>
<td>-</td>
</tr>
<tr>
<td>Synthetic oil</td>
<td>0.248</td>
<td>0.360</td>
<td>55</td>
</tr>
<tr>
<td>Silicone grease</td>
<td>0.248</td>
<td>0.110</td>
<td>38</td>
</tr>
</tbody>
</table>

The Beer–Lambert penetration depths and ablation damage thresholds are given in Table 1. The 10.6 and 1.06 $\mu m$ data are taken from previous work [1,3]. The data for 248 nm were determined gravimetrically, as per Fig. 2. Because of the insensitivity to the task of the balance used, the fluence threshold values are estimated to have an error of 50%, and are in the process of being refined with more sophisticated profilometric techniques.
The 4.99 eV photons supplied by the excimer have sufficient energy for direct breaking of the bonds of the two covalent compounds investigated [17,18], all being below this value. This is reflected in the low penetration depth (i.e. thus, high extinction coefficients) measured. The main interaction mode is, thus, taken to be bond scission.

Thermo-gravimetric results indicated a low boiling point for the synthetic oil, of 370 °C, with 16% by mass solid, black residue remaining. This substance was found to be relatively easily removed by all three laser systems. For the CO2 laser the beam couples sufficiently with the oil for direct heating to occur, while for the Nd:YAG, heating is indirect, by conduction from the metal surface [3]. From Table 1 it is clear that coupling is better than three orders of magnitude better at 248 nm than at 10.6 μm. In the infra-red, coupling is via excitation of vibrational modes, while in the UV, electronic excitation leading to bond breaking takes place. From an application point of view, all three lasers types are able to interact with low boiling organics, with the caveat that care should be taken to stay below the damage threshold for the...
substrate. This was more easily accomplished with the excimer, dominantly because of the short pulse width. It is of interest to report that no residue remained on the surface in the case of either the Nd:YAG or the CO₂ lasers. We regard the most probable explanation to be the rapidity of heating, relative to heating in a conventional furnace, causing evaporation sufficiently violent to remove all solid residues.

Thermo-gravimetric analysis revealed a main decomposition at 640 °C for the silicone grease, leaving a residue of 22% by mass, which we assumed to be an SiC/SiO₂ mix. Neither the CO₂ nor the Nd:YAG was able to volatilize the silicone. A sticky, black material remained in both cases. The excimer, on the other hand, lifts the silicone without any trace of residue visible to the eye or microscopically. The Si–C and Si–O bonds in silicone are less than the 4.99 eV of the excimer photons, making photolytic bond breaking the most probable interaction mode. Of practical interest is the temperature history of the alloy surface during treatment. Fig. 4 contains simulations of the temperatures profiles during the treatment of a Ti64 surface covered with a 150–200 nm thick silicone grease film. Note that in these figures, z refers to depth referenced to the interface; thus, z = 200 nm is the top of the contaminant surface film, and z = 0 is the position of the interface between contaminant and substrate. Photolytic ablation is obviously a highly non-equilibrium process [7], and the temperatures calculated for the silicone case as the maximum possible case for the ablated fragments. Despite this caution, we regard Fig. 4c as a fair enough reflection of reality to be used for practical applications. In practice, the Ti64 appears untouched, with only traces of silicon detectable by XPS as discussed below, and no evidence of oxidation. For the other two laser systems, temperatures high enough for the decomposition at 640 °C, but not high enough for volatilization of the solid. Interestingly, the enthalpy value calculated from the Beer–Lambert penetration depth and the fluence threshold of silica, indicates a thermal load of higher than that required for vapourizing silica and silicon carbide. Hence, in line with Dyer’s argument [17,18], the process should undoubtedly not be regarded as ‘cold’.

4.4. XPS measurement and surface chemistry

X-ray photo-electron spectroscopy was undertaken on Ti64 samples to determine the surface composition as received, and after laser treatment, to an accuracy to 0.1 at.% and a depth range of 2–10 nm. The as received samples were dominated by oxygen containing organic compounds, with low levels of titanium, titanium oxides and nitrogen with trace calcium silicon and iron. For the silicone grease contaminated Nd:YAG laser processed specimens the treatment did not alter the samples in any way, leaving the surface chemistry unchanged. For the contaminated Spectron CO₂ after laser treatment high levels of nitrogen containing organic material were still present, with the titanium surface detected as oxides and carbides indicating thermally induced reactions with the contaminants with oxidation. For the excimer trials hydraulic oil and silicone grease were applied, and were processed at high fluence (400 mJ cm⁻²) and low fluence (150 mJ cm⁻²), with argon shrouding. Post-treatment results showed organic fragment and free carbon levels significantly reduced, but a trace residue of silicon was detected as previously discussed.

5. Conclusions

A 1D model has been created that correlates the observed interaction modes for the three laser systems investigated. The model accounts of the beam–substrate and beam–contaminant interactions and predicts surface temperatures and oxidation levels. The results correlate to the experimental and analytical results obtained to date, although, further model calibration is planned. The model and experimental results provide a developing means of predicting the interaction of laser with different titanium alloys and possible contaminants of industrial interest.

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References


