Wettability characteristics of a mild steel modified with CO$_2$, Nd:YAG, excimer and high power diode lasers

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Abstract

Interaction of CO$_2$, Nd:YAG, excimer and high power diode laser (HPDL) radiation with the surface a common mild steel (EN8) was found to effect changes in the wettability characteristics of the steel, namely changes in the measured contact angle of certain liquids. Such changes were identified as being due to modifications to: (i) the surface roughness, (ii) changes in the surface oxygen content and (iii) changes in the surface energy of the mild steel. However, it was found that changes in the wettability characteristics of the mild steel were predominantly influenced by the surface roughness. To a much lesser extent surface O$_2$ content is also thought to play a role. The work has shown that the wettability characteristics of the selected mild steel could be controlled and/or modified with laser surface treatment. Moreover, the findings of this work strongly indicate the existence of a relationship between the change of the wetting properties of the mild steel and the laser wavelength.

Keywords: CO$_2$ laser, Nd:YAG laser, excimer laser, high power diode laser (HPDL), steel, surface energy, wettability

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1. Introduction

Comparisons of the differences in the beam interaction characteristics with various materials of the predominant materials processing lasers, the CO$_2$, the Nd:YAG and the excimer laser, are limited. Previously the main fundamental differences resulting from wavelength variations of CO, CO$_2$, Nd:YAG and excimer lasers for a number of materials processing applications have been detailed [1-4]. Likewise, such practical comparisons between these traditional materials processing lasers and the more contemporary high power diode laser (HPDL) are even fewer in number. Previously Schmidt et al. [5] compared the performance of CO$_2$, excimer and HPDL in the removal of chlorinated rubber coatings from concrete surfaces, noting wavelength dependant differences in the process performance. Additionally, Bradley et al. [6] compared the CO$_2$ and HPDL for the treatment of Al$_2$O$_3$-based refractory materials in terms of microstructure, observing wavelength dependant microstructural characteristics unique to each laser. In more comprehensive investigations, Lawrence et al. [7, 8] compared the effects of CO$_2$, Nd:YAG, excimer and HPDL radiation on the wettability characteristics of an Al$_2$O$_3$/SiO$_2$ based ceramic, noting that changes in the wettability characteristics of the material varied depending upon the laser type.

The interfacial phenomena of wetting is often the primary factor governing whether a coating will adhere and bond to a substrate in practical applications such as enamelling and thermal spray coating. To date, very little work exists pertaining to the use of lasers for altering the surface properties of materials in order to improve their wettability characteristics. Notwithstanding this, it is recognised within the currently published work that laser irradiation of material surfaces can effect their wettability characteristics. Previously Zhou et al. [9,10] have carried out work on laser coating of aluminium alloys with ceramic materials (SiO$_2$, Al$_2$O$_3$, etc.), reporting on the well documented fact that generated oxide layers often promote metal/oxide wetting. Furthermore, Heitz et al. [11], Henari et al. [12] and Olfert et al. [13] have found that excimer laser treatment of metals results in improved coating adhesion. The improvements in adhesion were attributed to the fact that the excimer laser treatment resulted in a smoother surface and as such enhanced the action of wetting. However, the reasons for these changes with regard to changes in the material’s surface morphology, surface composition and surface energy are not reported. In contrast, work on HPDL modification of the wettability characteristics of a number of different ceramic materials [14] has shown that the wettability performance is affected by changes in the surface roughness, the surface O$_2$ content and the surface energy.
This present work describes the beam interaction characteristics of 1 kW CO$_2$ laser, a 400 W Nd:YAG laser, a 5 W KrF excimer laser and a 1.2 kW HPDL with a common mild steel specifically in terms of the differing effects thereof on the wettability characteristics. These incorporate chiefly: contact angle variations, the differences in morphological and microstructural features, the surface composition, and the surface energy changes.

2. Experimental procedure

2.1. Materials processing procedures

The solid materials used as substrates in the wetting experiments were rectangular billets (50 x 100mm with a thickness of 3mm) of common engineering low carbon mild steel (EN8). The contact surfaces of the materials were used as-received in the experiments. The general laser processing experimental arrangement comprised of the defocused laser beams being fired back and forth across the surfaces of the mild steel by traversing the samples beneath the laser beam using the x- and y-axis of the CNC gantry table. The general operating characteristics of the lasers used in the study are detailed in Table 1. Both pulsed and CW lasers were used in the study, therefore, both the average power and the peak power of each laser will differ. So, in order to reasonably compare the effects of each laser on the wettability characteristics of the mild steel, the laser energy density (fluence) of each laser beam incident on the mild steel surface was set by manipulating the laser power density and traverse speed in the case of the CO$_2$ laser and the HPDL, and the laser power density, pulse width and frequency in the case of the Nd:YAG and excimer lasers, such that the energy density of each of the four lasers incident upon the mild steel surface was around 159 J/cm$^2$.

2.3. Contact angle and surface energy analysis procedure

To investigate the effects of laser radiation on the wetting and surface energy characteristics of the mild steel wetting experiments were conducted. The experiments were comprised of control experiments carried out using the sessile drop technique with a variety of test liquids with known surface energy properties. Thus it was possible to quantify any surface energy changes in the mild steel resulting from laser interaction.

The sessile drop control experiments were carried out, using human blood, human blood plasma, glycerol and 4-octanol. Details of the test liquids, along with their total surface energy ($\gamma$), dispersive ($\gamma^p$) and polar ($\gamma^n$) component values can be found elsewhere [14]. The experiments were conducted in atmospheric conditions at a temperature of 20°C. The droplets were released in a controlled manner onto the surface of the test substrate materials (laser
treated and untreated) from the tip of a micropipette, with the resultant volume of the drops being approximately $6 \times 10^{-3}$ cm$^3$. Each experiment lasted for three minutes with profile photographs of the sessile drops being obtained every minute. The contact angles were then measured with a mean value being subsequently determined. The standard deviation due to experimental error was calculated as being ±0.2°.

It was observed during the wetting experiments conducted with both the enamel and the control liquids that, throughout the period of the experiments, no discernible change in the magnitude of the contact angle was observed, indicating that thermodynamic equilibrium was established at the solid-liquid interface at the outset of the experiments. This is perhaps surprising when one considers the temperature effect on surface tension as described by Mayers [15]. However, results similar to those observed in this study have been described by Agathopoulos et al. [16].

For comparison purposes, enamel-mild steel wetting experiments were carried out in atmospheric conditions with molten droplets of the enamel (600°C). The temperature of the enamel throughout the experiments was measured using a Cyclops infrared pyrometer. The droplets were released in a controlled manner onto the surface of the mild steel (laser treated and untreated) from the tip of a micropipette, with the resultant volume of the drops being approximately $15 \times 10^{-3}$ cm$^3$. Profile photographs of the sessile enamel drop were obtained for every 60°C fall in temperature of the molten enamel drop, with the contact angle subsequently being measured, and a mean value being obtained. Again, the standard deviation due to experimental error was calculated as being ±0.2°.

3. Effects of laser radiation on contact angle characteristics

As one can see from Table 2, under the experimental laser parameters employed, laser irradiation of the surfaces of the mild steel samples resulted in changes in the contact angle. Table 2 shows clearly that such changes were dependent upon the laser used. It can be seen that in general, interaction of the mild steel with CO$_2$ and the excimer laser radiation resulted in marginal increases in the contact angle between the mild steel and the control liquids. In contrast, interaction of the mild steel with the Nd:YAG and HPDL beams resulted in the contact angle between the mild steel and the control liquids reducing.

3.1. Variations in surface roughness characteristics

According to Neumann [17, 18], a model similar to that for heterogeneous solid surfaces can be developed in order to account for surface irregularities, being given by a rearrangement of Wenzel’s equation:
\[
gamma_{sl} = \gamma_{sv} - \left( \frac{\gamma_b \cos \theta_w}{r} \right)
\]

where, \( r \) is the roughness factor defined as the ratio of the real and apparent surface areas and \( \theta \) is the contact angle for the wetting of a rough surface. Equation (1) shows clearly that if the roughness factor, \( r \), is large, that is the solid surface is smooth, then \( \gamma_{sl} \) will become small, thus, a reduction in the contact angle will be inherently realised by the liquid if \( \theta < 90^\circ \). In contrast, if \( \theta > 90^\circ \) then the opposite will be observed.

The various surface effects of the respective lasers on the mild steel are clearly discernible from Figure 1. From the microstructures shown in Figure 1 it would appear that in all instances of laser treatment, surface melting and resolidification to varying degrees was induced. Indeed, reductions in the surface roughness of the mild steel were observed (using a Taylor-Hobson Surtronic 3+ profileometer) after interaction with the Nd:YAG and the HPDL beams, reducing from an initial Ra value of 1.46\( \mu \)m to 1.25\( \mu \)m and 1.12\( \mu \)m respectively. However, interaction of the mild steel with the CO\(_2\) and excimer laser radiation occasioned the roughening of the mild steel surface, causing the surface roughness to increase to the respective Ra values of 2.58\( \mu \)m and 2.12\( \mu \)m. Indeed, Feng et al. [19] noted that under certain surface conditions, contact angle is inversely proportional the surface roughness.

### 3.2. Variations in surface oxygen content

The O\(_2\) content of a material’s surface is an influential factor governing the wetting performance of the material [20, 21]. Wetting is governed by the first atomic layers of the surface of a material. Thus, in order to determine element content of O\(_2\) at the surface of the mild steel, it was necessary to examine the surface using x-ray photoemission spectroscopy (XPS).

Clear differences in the surface O\(_2\) content of the mild steel after interaction with all the selected lasers were observed. Increases in the surface O\(_2\) content were experienced by the mild steel after interaction with CO\(_2\), the Nd:YAG and the HPDL beams, increasing from an initial value of 34.2atomic\% to 41.5atomic\%, 35.7atomic\% and 40.1atomic\% respectively. Conversely, interaction of the mild steel with excimer laser radiation resulted in the surface O\(_2\) content of the mild steel decreasing slightly to 32.8atomic\%.

### 4. Surface energy and the dispersive/polar characteristics

The intermolecular attraction which is responsible for surface energy, \( \gamma \), results from a variety of intermolecular forces whose contribution to the total surface energy is additive [22]. The
majority of these forces are functions of the particular chemical nature of a certain material, and as such the total surface energy comprises of $\gamma^p$ (polar or non-dispersive interaction) and $\gamma^d$ (dispersive component; since van der Waals forces are present in all systems regardless of their chemical nature). Therefore, the surface energy of any system can be described by [22]

$$\gamma = \gamma^d + \gamma^p$$

Similarly, $W_{ad}$ can be expressed as the sum of the different intermolecular forces that act at the interface [22]:

$$W_{ad} = W_{ad}^d + W_{ad}^p = 2\left(\gamma_{sv}^d \gamma_{lv}^d\right)^{1/2} + 2\left(\gamma_{sv}^p \gamma_{lv}^p\right)^{1/2}$$

By equating Equation (3) with the Young-Dupre Equation:

$$W_{ad} = \gamma_{lv} (1 + \cos \theta)$$

the contact angle for solid-liquid systems can be related to the surface energies of the respective liquid and solid by

$$\cos \theta = \frac{2\left(\gamma_{sv}^d \gamma_{lv}^d\right)^{1/2} + 2\left(\gamma_{sv}^p \gamma_{lv}^p\right)^{1/2}}{\gamma_{lv}} - 1$$

In accordance with studies conducted by Fowkes [22] and Agathopoulos et al. [16], it is possible to estimate reasonably accurately the dispersive component of the mild steel surface energy, $\gamma_{sv}^d$, by plotting the graph of $\cos \theta$ against $(\gamma_{lv}^d)^{1/2}/\gamma_{lv}$ in accordance with Equation (5) [22], with the value of $\gamma_{sv}^d$ being estimated by the gradient (=2($\gamma_{sv}^d$)^{1/2}) of the line which connects the origin (cos $\theta = -1$) with the intercept point of the straight line (cos $\theta$ against $(\gamma_{lv}^d)^{1/2}/\gamma_{lv}$) correlating the data point with the abscissa at cos $\theta = 1$. Figure 2 shows the best-fit plot of $\cos \theta$ against $(\gamma_{lv}^d)^{1/2}/\gamma_{lv}$ for the untreated and laser treated mild steel-experimental control liquids system.

A comparison of the ordinate intercept points of the untreated and laser treated mild steel-liquid systems is given in Figure 2. One can see clearly that the best-fit straight lines for the mild-steel-liquid systems of the Nd:YAG laser and especially the HPDL intercept the ordinate higher above the origin than those of the untreated, CO$_2$ laser and excimer laser treated mild steel samples. This is of great importance since interception of the ordinate close to the origin is characteristic of the dominance of dispersion forces acting at the mild steel-liquid interfaces of
the untreated and excimer laser treated samples, resulting in poor adhesion [22, 23]. On the other hand, an interception of the ordinate well above the origin is indicative of the action of polar forces across the interface, in addition to dispersion forces, hence improved wettability and adhesion is promoted [22, 23]. Furthermore, because none of the best-fit straight lines intercept below the origin, then it can be said that the development of an equilibrium film pressure of adsorbed vapour on the mild steel surface (untreated and laser treated) did not occur [22, 23].

Again, in accordance with studies conducted by Fowkes [22] and Agathopoulos et al. [16], it is not possible to determine the value of the polar component of the mild steel surface energy, $\gamma_{sv}^p$, directly from Figure 2. This is because the intercept of the straight line ($\cos \theta$ against $(\gamma_{sv}^d \gamma_{lv}^d)^{1/2}/\gamma_{lv}$) is at $(\gamma_{sv}^d \gamma_{lv}^d)^{1/2}/\gamma_{lv}$, and thus only refers to individual control liquids and not the control liquid system as a whole. However, it has been established that the entire amount of the surface energies due to dispersion forces either of the solids or the liquids are active in the wettability performance [22, 24]. As such, it is possible to calculate the dispersive component of the work of adhesion, $W_{ad}^d$, using only the relevant part of Equation (3) thus

$$W_{ad}^d = 2\left(\gamma_{sv}^d \gamma_{lv}^d\right)^{1/2}$$  \hspace{1cm} (6)

The results reveal that for each particular control liquid in contact with both the untreated and laser treated mild steel surfaces, both $W_{ad}$ and $W_{ad}^d$ are related by the straight line relationship

$$W_{ad} = aW_{ad}^d + b$$  \hspace{1cm} (7)

where $a$ and $b$ are constants unique to each control liquid system. Also, for the control test liquids used, a linear relationship between the dispersive and polar components of the control test liquids surface energies has been deduced which satisfies the equation

$$\left(\gamma_{lv}^p\right)^{1/2} = 1.3\left(\gamma_{lv}^d\right)^{1/2} + 1.15$$  \hspace{1cm} (8)

By introducing Equation (7) into Equation (3) and rearranging, then

$$W_{ad}^p = (a - 1)W_{ad}^d + b$$  \hspace{1cm} (9)

By combining Equation (9) with Equation (3) and differentiating with respect to $\left(\gamma_{lv}^d\right)^{1/2}$, then the following can be derived:
Thus, from the best-fit straight line plots of $W_{ad}$ against $W_{ad}^d$ for the mild steel when it is both untreated and laser treated, it was possible to determine the constants $a$ and $b$ for each separate condition of the mild steel. Since $\gamma_{sv}^d$ has already been determined for the untreated and laser treated mild steel from Figure 2, then it is possible to calculate $\gamma_{sv}^p$ for untreated and laser treated mild steel using Equation (10).

As one can see from Table 3, Nd:YAG laser, HPDL and excimer laser treatment of the surface of the mild steel effected small increases in the polar component of the surface energy $\gamma_{sv}^p$. Such increases in the polar component of the surface energy of the mild steel have a positive effect upon the action of wetting and adhesion.

5. Discussion of laser effected wettability characteristics modification

The results detailed previously show clearly that interaction of the mild steel with the selected industrial lasers has resulted in the contact angle formed between the control liquids altering to various degrees depending upon the laser type. Under the selected experimental laser operating parameters, interaction of the mild steel typically with the Nd:YAG and HPDL beams effected a decrease in the contact angle, whilst interaction of the mild steel with CO$_2$ and excimer laser radiation occasioned small increases in the contact angle. Such changes in the value of the contact angle are influenced, depending upon the laser used, primarily by:

1. Modifications to the Surface Roughness - Depending upon the laser used, in this instance the Nd:YAG laser and the HPDL, the particular experimental laser parameters employed resulted in the ideal degree of melting and resolidification of the mild steel surface being induced. This in turn resulted in a reduction of the surface roughness, thus directly reducing the contact angle, $\theta$.

2. Surface Roughening - Depending upon the laser used, in this case the CO$_2$ laser, the particular experimental laser parameters employed resulted in a degree of melting and resolidification of the mild steel surface being induced which was not conducive to surface smoothing. Also, in the case of the excimer laser the resultant ablation of the mild steel surface resulted directly in an increase in the surface roughness. In both instances the increase in the mild steel surface roughness resulted inherently in an increase in the contact angle, $\theta$. 

\[
(\gamma_{sv}^p)^{1/2} = \frac{(\gamma_{sv}^d)^{1/2} (a - 1)}{1.3}
\]
3. **Surface O\textsubscript{2} Content** - An increase in the surface O\textsubscript{2} content of the mild steel resulting from laser treatment is an influential factor in the promotion of the action of wetting, since an increase in surface O\textsubscript{2} content inherently effects a decrease in the contact angle, and vice versa.

4. **Increase in the Polar Component, \(\gamma^p\), of the Surface Energy** - Resulting from the melting and resolidification of the mild steel surface, thus creating a different microstructure that quite possibly improved the action of wetting and adhesion.

From Figure 1 it can be seen that microstructures of the CO\textsubscript{2}, Nd:YAG and HPDL treated samples appear to be indicative of melting and resolidification. Indeed, the microstructures of the Nd:YAG and HPDL treated samples are very similar in nature. However, the microstructure of the CO\textsubscript{2} laser treated sample differs greatly. It is surmised that in the instances of the Nd:YAG and HPDL treated samples, the optimum degree of surface melting is obtained, resulting in the minimum surface roughness. Similar laser induced surface smoothing effects were obtained by Nicolas et al. [25] and Henari et al. [12], who observed that excimer laser treatment of ceramics and metals could result in the generation of a smoother surface. In contrast, it is believed that in the instance of the CO\textsubscript{2} laser treated sample, where the surface of the mild steel has become roughened as a consequence of laser interaction, the roughening is occasioned as a result of excess energy being absorbed by the surface of the mild steel, leading therefore to a higher level of surface melting. This in turn causes micro-porosities and a generally rough surface profile.

Indeed, this supposition is borne out somewhat by Figure 3, which shows that the surface condition of the mild steel resulting from HPDL modification (with a number of different traverse speeds) greatly affected the measured contact angle between the mild steel and vitreous enamel (see Figure 4). As one can see from Figure 3, at relatively low traverse speeds excess energy is deposited on the surface of the mild steel resulting in a high level of surface melting. This in turn causes porosities and a generally rough surface profile. As the traverse speed increases, however, the energy deposited on the surface of the mild steel reduces. Accordingly the degree of surface melting reduces ultimately to the optimum degree, resulting in the minimum surface roughness, and contact angle, at around 1500 mm/min. Beyond this point the surface roughness, and contact angle, can be seen to increase, indicating that insufficient melting, and consequently smoothing, was achieved. Again, such results are in accord with those obtained by Feng et al. [19], who noted that under certain surface conditions, contact angle reduction was inversely proportional to surface roughness. Moreover, Olfert et al. [13] found that excimer laser treatment of steel surfaces greatly improved the adhesion of a zinc
coating. They asserted that laser treatment occasioned the smoothing of many of the high
to frequency surface features, resulting in more complete wetting by the zinc.

The CO\textsubscript{2} laser operates in the CW mode and consequently the laser operating parameters used
in the experiments were exactly the same as those of the HPDL in every way (power, beam
diameter, traverse speed, etc.), the only difference being, however, the laser wavelength. There
are many other factors that may quite possibly come into play, but since the microstructures
obtained after CO\textsubscript{2} (Figure 1(b)) and HPDL (Figure 1(d)) treatment were so different, then it is
perhaps reasonable to propose that these changes are the result of wavelength difference
affected beam absorption. What is more, the definite similarity between the microstructures
obtained after Nd:YAG (Figure 1(c)) and HPDL (Figure 1(d)) treatment indicate further the
existence of a wavelength relationship.

In contrast, as Figure 1(e) shows, interaction of the mild steel with excimer laser radiation did
not cause melting of the surface, but instead induced surface ablation which consequently
resulted in a slightly rougher surface. Thus an increase in the contact angle was effected.
Similar observations were made by Lawrence et al. [8] during surface treatment of a ceramic
compound using an excimer laser. Additionally, Kokai et al. [26] have concluded that, with
excimer laser parameters which are conducive to the production of plasma, as was the case with
the mild steel, then the surface roughness is increased as a result of plasma induced debris
redistributing on the surface and excessive thermally induced surface fractures and porosities.
Clearly, since plasma generation was observed, then surface roughening after excimer laser
irradiation was perhaps to be expected. However, Liu et al. [27], Nicolas et al. [25] and Henari
et al. [12], have reported that irradiating ZrO\textsubscript{2} with excimer laser radiation with energy densities
in excess of 2.7 J/cm\textsuperscript{2}, resulted in a reduction in surface roughness. Such reductions were
attributed to the fact that at these levels of energy density, melting of the ZrO\textsubscript{2} surface occurred.

By means of cross-sectional SEM analysis it was possible to determine the laser melt/ablation
depth for each laser. It was found that the depth of the laser melting, and in the case of the
excimer laser, the ablation region, varied significantly according to laser type. For the CO\textsubscript{2},
Nd:YAG and HPDL the melt depths were measured as 170\textmu m, 45\textmu m and 100\textmu m respectively,
whilst for the excimer laser the ablation depth was measured as 10\textmu m. Clearly, the differences
in laser melt/ablation depth obtained with the Nd:YAG and excimer lasers was an order of
magnitude smaller than those of the CO\textsubscript{2} or HPDL. The main reason for these large differences
are thought to be due to the pulsed nature of the beams of the Nd:YAG and excimer lasers, as
opposed to the CW nature of the CO\textsubscript{2} or HPDL beams. Since the interaction time of a pulsed
beam with a material is much shorter than that of a CW beam, then consequently the depth of
the laser melt/ablation region will be much smaller due to the reduced time afforded for heat
transfer.
It is also of great importance to consider the surface O₂ content of the mild steel before and after treatment with the selected lasers. Increases in the surface O₂ content were experienced by the mild steel after interaction with CO₂ laser, the Nd:YAG laser and the HPDL beams, whilst interaction of the mild steel with excimer laser radiation resulted in the surface O₂ content of the mild steel decreasing. Such a result is in agreement with the findings of a number of workers [28, 29], who have noted that for many materials, irradiation with an excimer laser beam creates defective energy levels, in particular the formation of O₂ vacancies.

From the previous discussion it is unclear whether after laser surface treatment the surface roughness, the microstructural changes or the O₂ content alone, or a combination thereof, are the principal factors, influencing the observed changes in the wettability characteristics of the mild steel. However, by grinding the surfaces of the untreated and laser treated mild steel samples down the 1µm, whilst still retaining a laser treated surface, it was thus possible to isolate the effects of surface roughness by rendering them non-effective, and investigate at least the effects of the microstructural changes and possibly those of the O₂ content.

An examination of the contact angle characteristics of the ground mild steel samples using only glycerol revealed that the contact angle was consistently around 30° across the range of samples. In addition, from an XPS analysis the O₂ content of the mild steel samples it was found that O₂ content of the untreated sample remained around the original value at 33.8atomic%. For the CO₂, the Nd:YAG and the HPDL treated samples, however, the O₂ content was found to have reduced to a level similar to that of the untreated sample (34.3atomic%, 32.8atomic% and 33.2atomic% respectively), whilst the excimer laser treated sample increased to a level similar to that of the untreated sample (34.0atomic%). Since the measured contact angles of the ground samples were consistently similar, despite the presence of the laser induced microstructures, then, combined with the fact that the O₂ content of the ground samples differed very little, it is evident from these findings that the surface roughness alone is the major factor governing the changes in the wettability characteristics of the mild steel.

6. Conclusion

Interaction of CO₂ laser Nd:YAG laser, high power diode laser (HPDL) and excimer laser radiation with the surface of the mild steel was found to effect changes in the wettability characteristics of the material. It was observed that interaction of the mild steel with Nd:YAG and HPDL radiation effected reductions in the contact angle. In contrast, interaction of the mild steel with CO₂ and excimer laser radiation resulted in a slight increase in the contact
angle. Such changes were identified as being primarily due to: (i) the generation of a smoother surface after Nd:YAG and HPDL treatment due to optimum surface melting and resolidification. (ii) the surface roughness of the mild steel increasing after interaction with CO₂ and excimer laser radiation due to excess surface melting and ablation respectively, which in turn resulted directly in an increase in the contact angle. (iii) changes in the surface O₂ content of the mild steel; increasing after interaction with CO₂, Nd:YAG and HPDL radiation due to surface melting, and decreased after interaction with the excimer laser due to the creation of defective energy levels. (iv) increases in the polar component of the surface energy resulting from the melting and resolidification of the mild steel surface, thus creating a different microstructure that quite possibly improved the action of wetting and adhesion. However, it was found that changes in the wettability characteristics of the mild steel appeared to be predominantly influenced by the surface roughness, whilst the microstructure appeared not to have any effect on the mild steel’s wetting properties. Additionally, surface O₂ content is also thought to play a minor role.

It is a distinct possibility that a wavelength dependance of the change of the wetting properties can be deduced from the findings of this work. This is apparent from the very similar properties of the surfaces irradiated with the Nd:YAG laser and the HPDL, the wavelengths of which vary by little more than 66nm. However, it is important to note the high degree to which beam mode (temporal and spatial) will influence the laser process. Nonetheless, the work has shown that under the chosen experimental laser operating parameters, changes in the wettability characteristics of the mild steel were seen to vary depending upon the laser type.
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Figure 1. Typical SEM surface images of the mild steel (a) before laser treatment and after laser interaction with (b) CO$_2$ laser, (c) Nd:YAG laser, (d) HPDL and (e) excimer laser radiation.

Figure 2. Typical plot of $\cos \theta$ against $\left( \gamma_d^d \right)^{1/2} / \gamma_h$ for the untreated and laser treated mild steel in contact with the test control liquids.

Figure 3. Relationship between surface roughness, contact angle (enamel) and traverse speed for the HPDL treated mild steel.

Figure 4. Contact angles for the enamel ($\pm 0.2^\circ$) on (a) the as-received mild steel surface, and (b) the HPDL treated mild steel surface (1500 mm/min traverse speed).
Figure 1

(a) [Image of surface texture at 2000x magnification with 10µm scale]

(b) [Image of surface texture at 2000x magnification with 10µm scale]

(c) [Image of surface texture at 2000x magnification with 10µm scale]

(d) [Image of surface texture at 2000x magnification with 10µm scale]

(e) [Image of surface texture at 2000x magnification with 10µm scale]
Figure 2

The figure shows a graph plotting the relationship between $\cos \theta$ and $\frac{\left( \gamma_{lv} \right)^{1/2}}{\gamma_{lv}}$, where $\gamma_{lv}$ is the interfacial tension between two liquids. The graph includes data points for Untreated, CO$_2$ Laser Treated, Nd:YAG Laser Treated, HPDL Treated, and Excimer Laser Treated samples, as well as data for Blood, Blood Plasma, 4-octanol, and Glycerol.
Figure 3

Contact Angle, $\theta$
Surface Roughness, $Ra$
Laser Power: 500 W
Shield Gas: Oxygen

Traverse Speed (mm/min)
Surface Roughness, $Ra$ ($\mu m$)
Contact Angle, $\theta$ (degrees)
Figure 4

(a) $\theta = 64^\circ$

(b) $\theta = 23^\circ$
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Table 1. Details of the selected industrial lasers used.

Table 2. Mean values of contact angles formed between the selected test liquids at 20°C and the mild steel before and after interaction with the selected lasers.

Table 3. Determined surface energy values for the mild steel before and after laser irradiation.
Table 1

<table>
<thead>
<tr>
<th>Operating Characteristic</th>
<th>CO₂</th>
<th>Nd:YAG</th>
<th>HPDL</th>
<th>Excimer</th>
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</tr>
<tr>
<td>Pulse Width</td>
<td>~</td>
<td>0.3 - 10 ms</td>
<td>~</td>
<td>20 ns</td>
</tr>
<tr>
<td>Repetition Rate</td>
<td>~</td>
<td>1 - 1000 Hz</td>
<td>~</td>
<td>1-55 Hz</td>
</tr>
<tr>
<td>Fibre Core Diameter</td>
<td>~</td>
<td>600µm</td>
<td>~</td>
<td>~</td>
</tr>
<tr>
<td>Mode of Operation</td>
<td>CW</td>
<td>Pulsed (rapid)</td>
<td>CW</td>
<td>Pulsed (multiple)</td>
</tr>
<tr>
<td>Beam Diameter/Size</td>
<td>6mm</td>
<td>6mm</td>
<td>3 x 6mm</td>
<td>1.8 x 1.8mm</td>
</tr>
</tbody>
</table>

Wavelength: CO₂ gas 10.6µm, Nd:YAG crystal 1.06µm, HPDL 940nm, Excimer 248nm
Maximum Average Output: CO₂ gas 1 kW, Nd:YAG crystal 400 W, HPDL 2.5 kW, Excimer 5 W
Maximum Pulse Energy: CO₂ gas ~, Nd:YAG crystal 70 J, HPDL ~, Excimer 35 mJ
Pulse Width: CO₂ gas ~, Nd:YAG crystal 0.3 - 10 ms, HPDL ~, Excimer 20 ns
Repetition Rate: CO₂ gas ~, Nd:YAG crystal 1 - 1000 Hz, HPDL ~, Excimer 1-55 Hz
Fibre Core Diameter: CO₂ gas ~, Nd:YAG crystal 600µm, HPDL ~, Excimer ~
Mode of Operation: CO₂ gas CW, Nd:YAG crystal Pulsed (rapid), HPDL CW, Excimer Pulsed (multiple)
Beam Diameter/Size: CO₂ gas 6mm, Nd:YAG crystal 6mm, HPDL 3 x 6mm, Excimer 1.8 x 1.8mm
Table 2

<table>
<thead>
<tr>
<th>Laser</th>
<th>Contact Angle, $\theta$ (degrees)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Blood</td>
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<tr>
<td>Untreated</td>
<td>55</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>60</td>
</tr>
<tr>
<td>Nd:YAG</td>
<td>54</td>
</tr>
<tr>
<td>HPDL</td>
<td>41</td>
</tr>
<tr>
<td>Excimer</td>
<td>57</td>
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</table>
Table 3

<table>
<thead>
<tr>
<th>Surface Energy Component</th>
<th>Untreated</th>
<th>CO₂</th>
<th>Nd:YAG</th>
<th>HPDL</th>
<th>Excimer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dispersive, ( \gamma_S^d ) (mJ/m²)</td>
<td>66.04</td>
<td>65.94</td>
<td>65.42</td>
<td>64.64</td>
<td>65.51</td>
</tr>
<tr>
<td>Polar, ( \gamma_S^p ) (mJ/m²)</td>
<td>4.17</td>
<td>3.83</td>
<td>4.24</td>
<td>6.59</td>
<td>4.02</td>
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</tbody>
</table>