Wettability Characteristics of Carbon 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 of a common mild steel (EN8) was found to effect changes in the wettability characteristics of the steel, namely changes in the measured contact angle. These modifications are related to changes in the surface roughness, changes in the surface oxygen content and changes in the surface energy of the mild steel. The wettability characteristics of the selected mild steel could be controlled and/or modified by laser surface treatment. A correlation between the change of the wetting properties of the mild steel and the laser wavelength was found.

Keywords: laser, HPDL, steel, wettability, surface roughness, contact angle

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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 few. Previously the fundamental differences resulting from wavelength variations of CO, CO_2, Nd:YAG and excimer lasers for a number of materials processing applications have been given [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 the wavelength dependent differences in the process performance. Additionally, Bradley et al. [6] compared the CO_2 and HPDL for the treatment of Al_2O_3-based refractory materials in terms of microstructure, observing differing wavelength dependent microstructural characteristics for each laser. In 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_2O_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. At present, very little work has been published with regard 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 its wettability characteristics. Previously Zhou et al [9, 10] have carried out work on laser coating of aluminium alloys with ceramic materials (SiO_2, Al_2O_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 were not reported. Notwithstanding this, 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 several industrial lasers: 1 kW CO_2 laser, 400 W Nd:YAG laser, 5 W KrF excimer laser and 1.2 kW HPDL with a common mild steel in terms of the wettability characteristics. These incorporate chiefly: contact angle variations, differences in morphological features, surface composition, and surface energy changes.

2. Theoretical background

When a drop of liquid is in contact with a solid surface, the final shape taken by the drop, and thus whether it will wet the surface or not, depends upon the relative magnitudes of the molecular forces that exist within the liquid (cohesive) and between the liquid and the solid (adhesive) [15]. The index of this effect is the contact angle, θ, which the liquid subtends with the solid. The adhesion intensity of a liquid to a solid surface is known as the work of adhesion, W_{ad}, and is related to the liquid surface energy, γ_{lv}, by the Young-Dupre equation:

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

The influence of the substrate surface roughness on the wetting contact angle is also of great importance, being described by Wenzel's equation:

$$r(\gamma_{sv} - \gamma_{sl}) = \gamma_{lv}\cos\theta_w \tag{2}$$

where, r is the roughness factor defined as the ratio of the real and apparent surface areas, γ_{sv} is the solid surface energy, γ_{sl} is the solid-liquid surface energy and θ_w is the contact angle for the wetting of a rough surface. Clearly, as Equation (2) shows, the influence of surface roughness on the contact angle is to affect an increase in the contact angle. Thus, the smoother the contact surface is, the smaller the contact angle will be.

The intermolecular attraction which is responsible for surface energy, γ, results from a variety of intermolecular forces whose contribution to the total surface energy is additive [16]. The majority of these forces are functions of the particular chemical nature of a certain material, and as such the total surface energy (γ) comprises of γ^p (polar or non-dispersive interaction) and γ^d (dispersive component). As such, W_{ad} can be expressed as the sum of the different intermolecular forces that act at the interface [16]:

$$W_{ad} = W_{ad}^d + W_{ad}^p = 2\left(\gamma_{sv}^d \gamma_{lv}^d\right)^{1/2} + 2\left(\gamma_{sv}^p \gamma_{lv}^p\right)^{1/2} \qquad (3)$$

By equating Equation (3) with Equation (1), the contact angle for solid-liquid systems can be related to the surface energies of the respective liquid and solid by

$$\cos\theta = \frac{2\left(\gamma_{sv}^d \gamma_{lv}^d\right)^{1/2} + 2\left(\gamma_{sv}^p \gamma_{lv}^p\right)^{1/2}}{\gamma_{lv}} - 1 \qquad (4)$$

In accordance with studies conducted by Fowkes [16] and Agathopoulos et al. [17], it is possible to reasonably estimate the dispersive component of the mild steel surface energy, γ_{sv}^d, by plotting the graph of cos θ against $(\gamma_{lv}^d)^{1/2}/\gamma_{lv}$ in accordance with Equation (4) [16]. The value of γ_{sv}^d is then estimated from the gradient of the line which connects the origin with the intercept point of the straight line correlating the data point with the abscissa at cos $\theta = 1$.

As affirmed by the work of Fowkes [16] and Agathopoulos et al. [17], it is not possible to determine the value of the polar component of the mild steel surface energy, γ_{sv}^p, directly. This is because the intercept of the straight line 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 [16, 18]. It is therefore possible to calculate the dispersive component of the work of adhesion, W_{ad}^d, from Equation (3). Indeed, for each particular control liquid in contact with both the untreated and laser treated mild steel surfaces, W_{ad} has been correlated with W_{ad}^d by a linear relationship. Thus the following can be derived [8]:

$$\left(\gamma_{sv}^p\right)^{1/2} = \frac{\left(\gamma_{sv}^d\right)^{1/2}(a-1)}{1.3} \qquad (5)$$

From a plot of the linear relationship between W_{ad} and W_{ad}^d, a (the gradient of the relationship between W_{ad} and W_{ad}^d) can be determined for the untreated and laser treated mild steel.

3. Experimental procedures

The general operating characteristics of the lasers used in the study are detailed in Table 1. For all experiments the assist gas used was O_2. Both pulsed and CW lasers were employed, therefore, both the average power and the peak power of each laser will differ. Thus the laser energy density (fluence) of each laser beam was set such that the laser power densities, interaction times and traverse speeds of each laser was 159 J/cm^2.

The liquids used for the wetting experiments were human blood, human blood plasma, glycerol and 4-octanol. The test liquids, along with their total surface energy (γ_2) as well as the dispersive (γ_2^d) and polar (γ_2^p) components, are detailed elsewhere [14]. 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 wetting experiments were carried out in atmospheric conditions at room temperature. The droplets were released in a controlled manner onto the surface of the test substrate materials (treated and untreated) from the tip of a micropipette, with the resultant volume of each drop being approximately 6×10^{-3} cm^3. Each experiment lasted for three minutes with profile photographs of the sessile drops taken at minute intervals, with the contact angle subsequently being measured. The experimental results showed that throughout the period of the tests no discernible change in the magnitude of the contact angle occurred.

Surface analysis of the samples after laser treatment was conducted using scanning electron microscopy (SEM) and x-ray photoemission spectroscopy (XPS), with surface roughness measurements being obtained using a Taylor-Hobson (Surtronic 3+) profileometer.

4. Results

As one can see from Table 2, laser irradiation of the surfaces of the mild steel samples resulted in changes in the contact angle depending upon the laser used. One possible reason for this is that the surfaces obtained after laser treatment are altered considerably; being smoother than the original untreated surface (1.46μm), in the case of the HPDL (1.12μm and the Nd:YAG laser (1.25μm), and rougher in the case of the CO_2 (2.58μm) and excimer lasers (2.12μm). As Equation (2) shows, if the roughness factor, r, is large, that is the solid surface is smooth, then γ_{sl} will become small, thus, a reduction in the contact angle will be inherently realised by the liquid if $\theta < 90^0$ [16].

Figure 2 shows the best-fit plot of cos θ against $(\gamma_{lv}^d)^{1/2}/\gamma_{lv}$ for the untreated and laser treated mild steel-experimental control liquids system. As discussed above, it is possible to determine directly from Figure 2 the dispersive component of the mild steel surface energy, γ_{sv}^d. The values subsequently obtained for γ_{sv}^d, as well as those calculated for γ_{sv}^p using Equation (5) are shown in Table 2.

The O_2 content of a material's surface is another influential factor in the wetting performance of the material [19, 20]. Wetting is governed by the first atomic layers of the surface of a material. Thus, in order to determine the content of O_2 on the surface of the mild steel XPS analysis was used. The surface O_2 content was found to increase after interaction with the CO_2, Nd:YAG and HPDL beams from an

initial value of 34.2% to 41.5%, 35.7% and 40.1% respectively. Conversely, interaction of the mild steel with excimer laser radiation resulted in the surface O_2 content decreasing to 32.8%.

5. Discussion

In the instances where the surface of the mild steel has become roughened as a consequence of laser interaction, it is thought that the roughening is occasioned as a result of excess energy being absorbed by the surface of the mild steel, leading therefore to a high level of surface melting. As was observed from a SEM analysis, this in turn caused micro-porosities and a generally rough surface profile. In the case of the excimer laser, singularly, the laser radiation did not cause melting of the surface, but instead induced surface ablation which consequently resulted in a rough surface. Kokai et al. [21] 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 redepositing on the surface and excessive thermally induced surface fractures and porosities. Since plasma generation was observed, then surface roughening after excimer laser irradiation was perhaps to be expected.

In contrast, the surface smoothing of the mild steel after HPDL interaction is caused as a result of the surface absorbing a level of energy such that an adequate degree of surface melting occurs. Accordingly, a minimum surface roughness, and thus contact angle, is achieved. Similar laser induced surface smoothing effects were obtained by Nicolas et al. [22] and Henari et al. [12], who observed that excimer laser treatment of ceramics and metals could result in the generation of a smoother surface. Olfert et al. [13] found also 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 frequency surface features, resulting in more complete wetting by the zinc.

A comparison of the ordinate intercept points of the untreated and laser treated mild steel-liquid systems in Figure 2 shows that for the mild steel-liquid systems of the HPDL and Nd:YAG laser treated mild steel samples the ordinate intercept is higher above the origin than those of the untreated, CO_2 and excimer laser treated mild steel samples. This is indicative of the increased action of polar forces across the interface, in addition to dispersion forces, in the HPDL and Nd:YAG laser treated mild steel. Hence improved wettability and adhesion is promoted [16, 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 [16, 23].

6. Conclusion

Interaction of CO_2, Nd:YAG, excimer and high power diode laser (HPDL) radiation with the surface of the mild steel was found to effect changes in the wettability characteristics of the material. Such changes were identified as being primarily due to: modifications to the surface roughness, changes in the surface oxygen content and changes in the surface energy of the mild steel. A wavelength dependence of the change of the wetting properties can be deduced from the findings of this work.

References

1. F. Dausinger, Proc. of ECLAT' 90: Laser Treatment of Materials 1 (1990) 1.
2. S. Shuttleworth, App. Surf. Sci. 96-98 (1996) 513 .
3. P.E. Dyer, J. Gonzalo, P.E. Key, D. Sands, M.J.J. Schmidt, App. Surf. Sci. 110 (1997) 345.
4. X. Chen, W.T. Lotshaw, A.L. Ortiz, P.R. Staver, C.E. Erikson, J. of Laser Apps. 8 (1996) 233.
5. M.J.J. Schmidt, L. Li, J.T. Spencer, App. Surf. Sci. 138-139 (1998) 378.
6. L. Bradley, L. Li, F.H. Stott, App. Surf. Sci. 138-139 (1998) 522.
7. J. Lawrence, L. Li, J.T. Spencer, Proc. of ICALEO' 98: Laser Materials Processing 85D (1998) 76.
8. J. Lawrence, L. Li, J. Phys. D. 32 (1999) 1075.
9. X.B. Zhou, J.T.M. Dehosson, J. de Phys. IV 3 (1993) 1007.
10. X.B. Zhou and J.T.M. Dehosson, Acta Metall. Mater. 42 (1994) 1155.
11. J. Heitz, E. Arenholz, T. Kefer, D. Bäuerle, H. Hibst, A. Hagemeyer, App. Phys. A 55 (1992) 391.
12. F. Henari, W. Blau, App. Optics, 34 (1995) 581.
13. M. Olfert, W. Duley, T. North, Laser Processing: Surface Treatment and Film Deposition, Kluwer Academic Publishers, (1996) p. 479.
14. J. Lawrence, L. Li, J.T. Spencer, App. Surf. Sci. 138-139 (1998) 195.
15. M.J. Jaycock, G.D. Parfitt, Chemistry of Interfaces, Wiley, NY, p. 234.
16. F.M. Fowkes, Ind. Eng. Chem. 56 (1964) 40.
17. S. Agathopoulos, P. Nikolopoulos, J. of Biomed. Mater. Res. 29 (1995) 421.
18. R.J. Good, L.A. Girifalco, J. Phys. Chem. 64 (1960) 561.
19. M. Ueki, M. Naka, I. Okamoto, J. Mat. Sci. Lett. 5 (1986) 1261.
20. J.G. Li, Rare Metals 12 (1993) 84.
21. F. Kokai, K. Amano, H. Oat, F. Umemura, App. Phys. A 54 (1992) 340.
22. G. Nicolas, M. Autric, W. Marine, G.A. Shafeev, App. Surf. Sci., 109-110 (1997), 289.
23. D.K. Chattoraj, K.S. Birdi, Adsorption and the Gibbs Surface Excess, Plenum Press, p. 95.

LIST OF FIGURES

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

Fig. 1
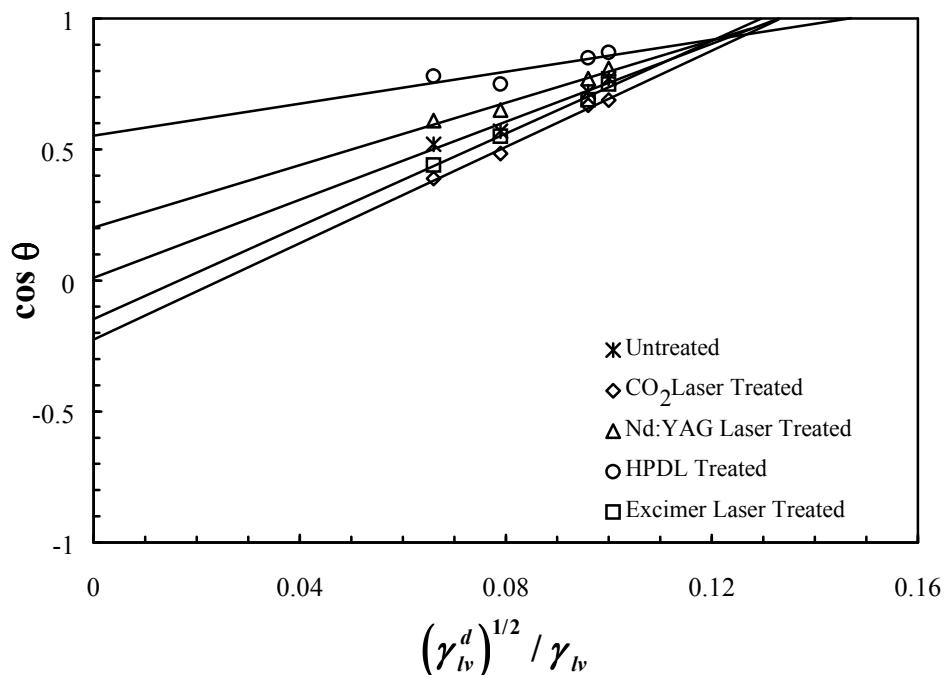
LIST OF TABLES

Table 1. Details of the selected industrial lasers used.

Table 2 : Measured contact angle values for the mild steel before and after laser irradiation.

Table 3 : Measured surface energy values for the mild steel before and after laser irradiation.

Table 1

| Operating Characteristic | Industrial Laser | | | |
	CO_2	Nd:YAG	HPDL	Excimer
Wavelength	10.6μm	1.06μm	940nm	248nm
Maximum Average Output	1 kW	400 W	1.2 kW	5 W
Maximum Pulse Energy	~	70 J	~	35 mJ
Pulse Width	~	0.3 - 10 ms	~	20 ns
Repetition Rate	~	1 - 1000 Hz	~	1-55 Hz
Fibre Core Diameter	~	600μm	~	~
Mode of Operation	CW	Pulsed (rapid)	CW	Pulsed (multiple)

Table 2

| Laser | Contact Angle, θ (degrees) | | | |
	Blood	Plasma	Glycerol	4-octanol
Untreated	55	59	44	40
CO_2	60	67	51	49
Nd:YAG	54	48	43	37
HPDL	41	39	32	30
Excimer	57	64	46	41

Table 3

| Surface Energy Component | Laser | | | | |
	Untreated	CO_2	Nd:YAG	HPDL	Excimer
Dispersive, (γ_{sv}^{d}) (mJ/m^2)	66.04	65.94	65.42	64.64	65.51
Polar, (γ_{sv}^{p}) (mJ/m^2)	4.17	3.83	4.24	6.59	4.02