

# **A laser-based technique for the coating of mild steel with a vitreous enamel**

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## **Abstract**

Marked changes in the wettability characteristics of EN8 mild steel were observed after high power diode laser (HPDL) surface treatment of the metal. The morphological, microstructural and wetting characteristics of the steel were determined using optical microscopy, scanning electron microscopy (SEM), X-ray photoemission spectroscopy (XPS) and wetting experiments by the sessile drop technique. Improvements in the wetting action of the mild steel after HPDL surface treatment were identified as being the result of: The HPDL induced melting of the mild steel surface which brought about a reduction of the surface roughness; The small increase in the polar component of the surface energy and the increase in the surface O<sub>2</sub> content of the mild steel resulting from HPDL treatment. This work has demonstrated that the use of HPDL radiation to alter the wetting characteristics of mild steel in order to facilitate improved enamelling is a real possibility.

*Keywords:* High power diode laser (HPDL); Mild steel; Enamel; Wettability; Coating; Glaze

## 1. Introduction

Wetting is often the primary factor governing whether or not a coating will adhere and bond to a substrate. In practical applications where vitreous enamels are fired onto mild steels, the performance of the article is directly linked to the nature of the enamel-steel interface. Consequently, both scientists and engineers alike have a great interest in understanding the interfacial phenomena between vitreous enamels and mild steels. Many studies to investigate these phenomena have been carried out, however, they have been principally concerned with the wettability of zirconia and other oxide ceramics on metals [1-5], as well as the adhesion of silicone sealants to aluminium [6] and the coating of aluminium alloys with ceramic materials [7, 8]. The interfacial mechanisms investigated have centred principally around the thermodynamic criterion [2, 3, 5], the electronic theory [4] and the occurrence of oxidation [1, 9].

Lasers can offer the user not only an exceedingly high degree of process controllability, but also a great deal of process flexibility. Yet at present, very little published work exists pertaining to the use of lasers for altering the surface properties of materials in order to improve their wettability characteristics. Nevertheless, it is recognised within the currently published work that laser irradiation of a metal surface can bring about changes in the metal's wettability characteristics. Previously Zhou et al. [7, 8] have carried out work on laser coating of aluminium alloys with ceramic materials ( $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ , etc.), reporting on the well documented fact that generated oxide layers often promote metal/oxide wetting. Also, Heitz et al. [10] and Olfert et al. [11] 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, Lawrence and Li have amply demonstrated the practicability of employing different types of lasers to effect changes in the wettability characteristics of ceramics [12-14] and metals [15, 16] for improved adhesion and bonding.

This present work details the use of a novel 1.2 kW high power diode laser (HPDL) to alter the wettability characteristics of a common engineering mild steel, and the effects thereof on the adhesion and bonding characteristics with a vitreous enamel. The intention being to facilitate the hitherto impossible task of enamelling mild steel in normal atmospheric conditions without pre-treatment of the steel. Indeed, such a process has been employed by the authors to enable the sealing, by means of laser enamelling, of ceramic tile grouts [17-19].

## 2. Experimental procedures

The laser used in the study was a 1.2 kW HPDL (Rofin-Sinar, DL-012), emitting at 940 nm. The laser beam was focused directly onto the samples to a 6 mm x 20 mm rectangular beam with a fixed power of 500 W. The laser head assembly and focusing optics are shown schematically in Fig. 1. The beam was traversed across the samples by means of mounting the assembly head onto the z-axis of a 3-axis CNC table. The focused laser beam was thus fired across the surface of the mild steel by traversing the samples beneath the laser beam using the x- and y-axis of the CNC table at speeds of 250-2000 mm/min, whilst 8 l/min of coaxially blown O<sub>2</sub> gas was used to assist the surface treatment process.

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 ( $\gamma_2$ ) as well as the dispersive ( $\gamma_2^d$ ) and polar ( $\gamma_2^p$ ) components, are detailed elsewhere [13]. An additional set of wetting experiments were conducted to simply determine the contact angle between the enamel and the mild steel before and after laser treatment.

The solid materials used as substrates in the wetting experiments were rectangular billets (50 x 100 mm<sup>2</sup> with a thickness of 3 mm) 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 a temperature of 20°C. The droplets were released in a controlled manner onto the surface of the mild steel substrate (treated and untreated) from the tip of a micropipette, with the resultant volume of the drops being approximately 6 x 10<sup>-3</sup> cm<sup>3</sup>. Each experiment lasted for three minutes with profile photographs of the sessile drops being obtained every minute, with the contact angle subsequently being measured using Vislog 5 image processing software to an accuracy of ±0.1°. The experimental results showed that throughout the period of the tests no discernible change in the magnitude of the contact angle occurred.

## 3. Contact angle and wettability characteristics

An optical micrograph of a sessile drop of enamel (20°C) placed on the surface of the mild steel before (a) and after (b) HPDL irradiation with the contact angle superimposed is shown in Fig. 2. The HPDL modified sample depicted in Fig. 2 was treated with a laser power of 500 W at a rate of 1500 mm/min in an O<sub>2</sub> atmosphere. As one can see from Fig. 2, HPDL irradiation of the mild steel surface effected a considerable reduction in the enamel contact angle.

### 3.1. The effects of surface roughness

One explanation for this observed reduction in the enamel contact angle is that the surface obtained after laser treatment was somewhat smoother than the original untreated surface. The influence of the substrate surface roughness on the wetting contact angle is also of great importance, being described by Wenzel's equation:

$$r(\gamma_{sv} - \gamma_{sl}) = \gamma_{lv} \cos \theta_w \quad (1)$$

where,  $r$  is the roughness factor defined as the ratio of the real and apparent surface areas,  $\gamma_{sv}$  is the solid surface energy,  $\gamma_{sl}$  is the solid-liquid surface energy and  $\theta_w$  is the contact angle for the wetting of a rough surface. Clearly, as Eq. (1) 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 mean surface roughness (Ra) value of the surface of the as-received mild steel was 1.46  $\mu\text{m}$ , whilst for the HPDL treated mild steel surface the mean Ra value was 1.12  $\mu\text{m}$ . Similar laser induced surface smoothing effects were obtained by Nicolas et al. [20] and Henari et al. [21], who observed that excimer laser treatment of ceramics and metals could result in the generation of a smoother surface. Therefore, according to Eq. (1), the smoother surface will inherently result in a reduction in the contact angle.

Indeed, this fact is borne out somewhat by Fig. 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. As one can see from Fig. 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. Such results are in accord with those obtained by Feng et al. [22], who noted that under certain surface conditions, contact angle reduction was inversely proportional to surface roughness. Moreover, Olfert et al. [11] 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 frequency surface features, resulting in more complete wetting by the zinc.

### 3.2. The effects of surface $O_2$ content

In addition to the above, the improvement in the wetting action experienced by the mild steel can be ascribed in some part to the increase in the surface O<sub>2</sub> content of the mild steel following HPDL treatment; since this is known to increase the likelihood of wetting [1, 9]. Indeed, since wetting is governed by the first atomic layers of the surface of a material, the O<sub>2</sub> content at the surface of the mild steel before and after HPDL treatment was determined using XPS. In a sample treated with a laser power of 500 W at a rate of 1500 mm/min and in an O<sub>2</sub> atmosphere, the surface O<sub>2</sub> content was found to have increased after HPDL treatment from 34at% to 40at%. Clearly, oxidation of the HPDL treated surface of the mild steel has occurred. This indicates that O<sub>2</sub> enrichment of the laser treated mild steel surface was active in promoting wetting and adhesion [1, 9].

### 3.3. Surface energy and its dispersive/polar characteristics

The adhesion energy of a liquid to a solid surface (the work of adhesion),  $W_{ad}$ , is given by the Young-Dupre equation:

$$W_{ad} = \gamma_{lv}(1 + \cos\theta) \quad (2)$$

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 [23]. The majority of these forces are functions of the particular chemical nature of a certain material, and as such the total surface energy ( $\gamma$ ) comprises of  $\gamma^p$  (polar or non-dispersive interaction) and  $\gamma^d$  (dispersive component). Therefore, the surface energy of any system may be described by [23]

$$\gamma = \gamma^d + \gamma^p \quad (3)$$

As such,  $W_{ad}$  can be expressed as the sum of the different intermolecular forces that act at the interface [23]:

$$W_{ad} = W_{ad}^d + W_{ad}^p = 2(\gamma_{sv}^d \gamma_{lv}^d)^{1/2} + 2(\gamma_{sv}^p \gamma_{lv}^p)^{1/2} \quad (4)$$

By equating Eq. (4) with Eq. (2), the contact angle for solid-liquid systems can be related to the surface energies of the respective liquid and solid by

$$\cos\theta = \frac{2(\gamma_{sv}^d \gamma_{lv}^d)^{1/2} + 2(\gamma_{sv}^p \gamma_{lv}^p)^{1/2}}{\gamma_{lv}} - 1 \quad (5)$$

It is possible to estimate the dispersive component of the mild steel's surface energy,  $\gamma_{sv}^d$ , by using Eq. (5), and plotting the graph of  $\cos \theta$  against  $(\gamma_{lv}^d)^{1/2}/\gamma_{lv}$ . Fig. 4 shows the best fit plots for the untreated and HPDL treated steel. The laser parameters used were a laser power of 500 W, a rate of 1500 mm/min and an O<sub>2</sub> atmosphere. The surface roughness and surface O<sub>2</sub> content resulting from processing under these conditions were 1.12  $\mu\text{m}$  and 40at% respectively. Thus the value of  $\gamma_{sv}^d$  is 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  $\cos \theta = 1$  [24]. The value of  $\gamma_{sv}^d$  for the untreated and HPDL treated (1500 mm/min traverse speed) mild steel is shown in Table 1. From the best-fit plots of  $\cos \theta$  against  $(\gamma_{lv}^d)^{1/2}/\gamma_{lv}$ , it was found that the ordinate intercept point of the untreated mild steel-liquid system was closer to  $\cos \theta = -1$  than that of the HPDL treated mild steel-liquid system. This indicates that, in principle, dispersion forces are acting mainly at the mild steel-liquid interface, resulting in poor adhesion [24, 25]. In contrast, the best-fit straight line for the HPDL treated mild steel-liquid system intercepted the ordinate considerably higher above the origin. This is indicative of the action of polar forces across the interface, in addition to dispersion forces, hence improved wettability and adhesion is promoted [24, 25].

It is not possible to determine the value of the polar component of the mild steel's surface energy,  $\gamma_{sv}^p$ , directly from plots of  $\cos \theta$  against  $(\gamma_{lv}^d)^{1/2}/\gamma_{lv}$ . This is because the intercept of the straight line ( $\cos \theta$  against  $(\gamma_{lv}^d)^{1/2}/\gamma_{lv}$ ) is at  $2(\gamma_{sv}^p \gamma_{lv}^p)^{1/2}/\gamma_{lv}$ , and thus only refers to individual control liquids and not the control liquid system. 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 [24, 26]. It is therefore possible to calculate the dispersive component of the work of adhesion,  $W_{ad}^d$ , from Eq. (4). The results revealed that for each particular control liquid in contact with both the untreated and laser treated mild steel surfaces,  $W_{ad}$  could be correlated with  $W_{ad}^d$  by a linear relationship.

$$W_{ad} = aW_{ad}^d + b \quad (6)$$

where  $a$  and  $b$  are constants unique to each control liquid system. A linear relationship between the dispersive and polar components of the control test liquids surface energies exists, thus

$$(\gamma_{lv}^p)^{1/2} = 0.45(\gamma_{lv}^d)^{1/2} + 1.3 \quad (7)$$

By introducing (6) into (3) and rearranging, then

$$W_{ad}^p = (a - 1)W_{ad}^d + b \quad (8)$$

or

$$\left(\gamma_{sv}^p\right)^{1/2} \left(\gamma_{lv}^p\right)^{1/2} = (a - 1) \left(\gamma_{sv}^d\right)^{1/2} \left(\gamma_{lv}^d\right)^{1/2} + \frac{b}{2} \quad (9)$$

By introducing (7) into (9) and differentiating with respect to  $\left(\gamma_{lv}^d\right)^{1/2}$ , considering that  $\left(\gamma_{sv}^d\right)^{1/2}$  and  $\left(\gamma_{sv}^p\right)^{1/2}$  are constant, then the following is valid:

$$\left(\gamma_{sv}^p\right)^{1/2} = \frac{\left(\gamma_{sv}^d\right)^{1/2} (a - 1)}{1.3} \quad (10)$$

Since  $\gamma_{sv}^d$  has already been determined for the untreated and laser treated mild steel from the plots of Eq. (5), it is possible to calculate  $\gamma_{sv}^p$  for untreated and laser treated mild steel using Eq. (10) (see Table 1).

As Table 1 clearly shows, HPDL treatment of the surface of the mild steel has led to a small increase in the polar component of the surface energy,  $\gamma_{sv}^p$ , thus improving the action of wetting and adhesion. It is surmised that this increase may be due to HPDL induced changes in the surface microstructure of the mild steel.

It is important to note that because of the long range ionic interactions in the mild steel and the composite nature of the interfaces between the mild steel and the control liquids, it is highly likely that the thermodynamically defined total solid surface energy,  $\gamma$ , as defined in Eq. (3), will be higher than the sum of the dispersive,  $\gamma^d$ , and the polar,  $\gamma^p$ , components of the surface energy. Although the increase in (excess) surface free energy will probably be less than the increase in the total lattice energy. On the other hand, an absorbed liquid layer may shield the ionic fields substantially. As such, all the data derived from Equations (4) - (10) should be considered as being semi-empirical. Notwithstanding this, as the studies by Gutowski et al.[6] and Agathopoulos et al. [14] found, it is reasonable to conclude from the data obtained from Equations (4) - (10) that HPDL treatment of the mild steel surface has caused a small increase in the polar component,  $\gamma^p$ , of the surface energy.

#### 4. Conclusions

High power diode laser (HPDL) surface treatment of the EN8 mild steel resulted in changes in the wettability characteristics of the mild steel and the enamel. Improvements in the wetting action of the mild steel after HPDL surface treatment were identified as being the result of a number of factors. Firstly, the HPDL induced melting of the mild steel surface which brought about a reduction of the surface roughness, thus directly reducing the contact angle,  $\theta$ . Secondly, the small increase in the polar component of the surface energy,  $\gamma_{sv}^p$ , after HPDL treatment (which is thought to be due to the HPDL effected microstructural changes), thus improving the action of wetting and adhesion. Finally, the increase in the surface O<sub>2</sub> content of the mild steel resulting from HPDL treatment was identified as further promoting the action of wetting. This work demonstrates that it is distinctly possible to alter the wetting characteristics of the selected mild steel using the HPDL.

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## List of Figures

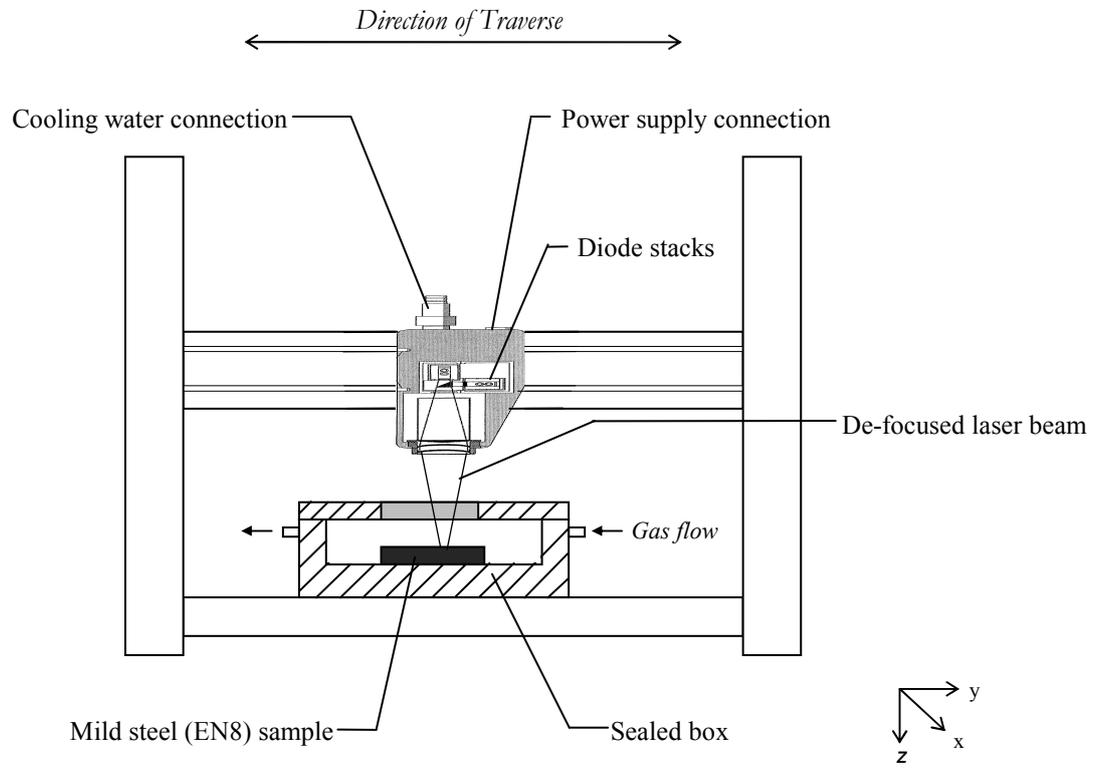
Fig.1. Schematic representation of the 1.2 kW HPDL head assembly.

Fig. 2. Contact angles for the enamel on (a) the as-received mild steel surface, and (b) the HPDL treated mild steel surface (1500 mm/min traverse speed).

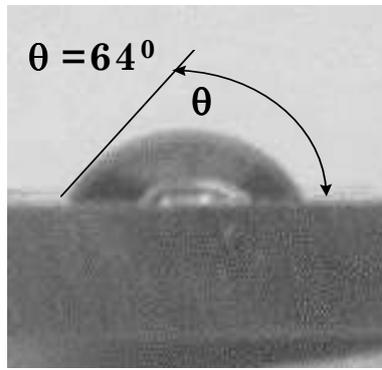
Fig. 3. Relationship between surface roughness, contact angle and traverse speed for the mild steel.

Fig. 4. Plot of  $\cos \theta$  against  $(\gamma_{lv}^d)^{1/2} / \gamma_{lv}$  for the untreated and HPDL treated mild steel in contact with the wetting test control liquids.

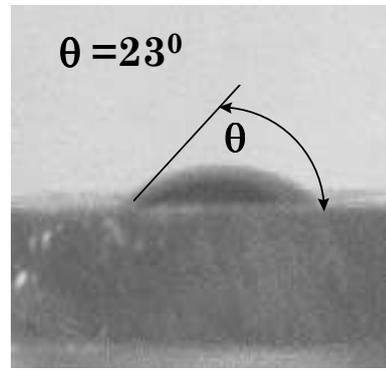
**Fig. 1**



**Fig. 2**



(a)



(b)

Fig. 3

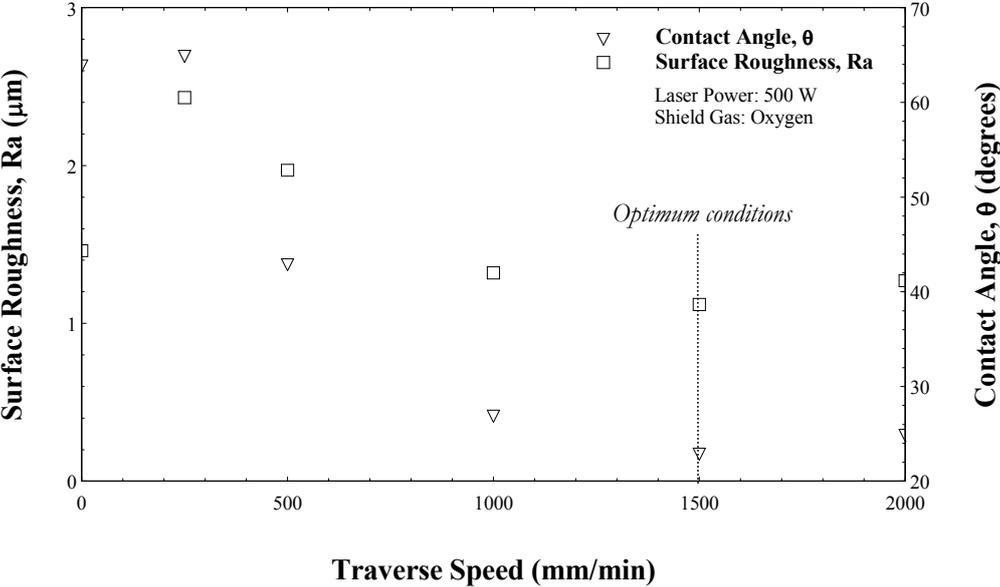
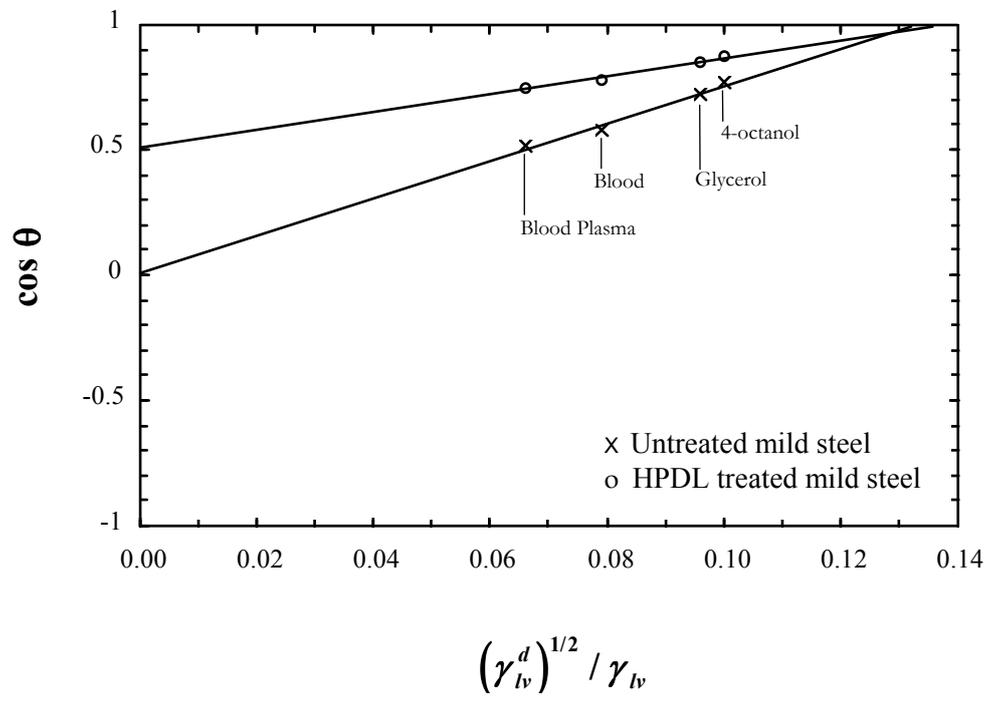


Fig. 4



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

**Table 1**

| <b>Characteristic</b>                     | <b>Untreated Mild Steel</b> | <b>HPDL Treated Mild Steel</b> |
|---|-----------------------------|--------------------------------|
| Dispersive Component, ( $\gamma_{sw}^d$ ) | 64.6 mJ/m <sup>2</sup>      | 66.2 mJ/m <sup>2</sup>         |
| Polar Component, ( $\gamma_{sw}^p$ )      | 4.2 mJ/m <sup>2</sup>       | 6.6 mJ/m <sup>2</sup>          |