Corrosion Protection of Carbon Steel by ND-YAG LASER

Basheer A. Abdul-Hussein
Chemical Engineering Department, University of Technology
Al-Sinaa'a St.52, Baghdad, IRAQ
00964 7901361896 basheer510@yahoo.com

ABSTRACT
Pulse ND-YAG laser was used to study the electrochemical behavior of low carbon steel in 1, 2, and 3.5 % NaCl solution before and after laser surface treatment (LST). Potentiostatic technique and Tafel extrapolation were performed in order to find the corrosion rates and the corrosion potential. The results show that the corrosion rates of LST were lower than that of untreated surface. The corrosion potential was moving in more positive direction, showing the decrease in cathodic reactivity. AFM, hardness test, and XRD were used to study the surface of carbon steel before and after LST, it's found that the roughness and hardness increase after LST. The XRD test indicates that the surface after LST is more pure than that obtained before LST.

Keyword: ND-YAG Laser, carbon steel, corrosion, protection

INTRODUCTION
Laser surface treatment prepares important effort for improvement in surface properties, such as corrosion performance and wear resistance. However, this technique has not been widely used for large area components in industrial applications because of the difficulty of cover large area of the metal with microstructural and compositional homogeneity (Chong et al, 2013).

A different way of improving the corrosion resistance of carbon steel is by laser surface melting (LSM). This technology is able to modify the corrosion resistance of carbon steel, as shown by a number of authors (Cristiano Padovani et al, 2011; Xin Tong et al, 2012; Pengyu et al, 2013). Treating a metal surface with laser irradiation can produce a resolidified layer in which precipitates are dissolved and redistribution of alloying elements takes place; according to the level of microsegregation achieved in the resolidified layer, variation in corrosion resistance of the metal is obtained after LSM (Chong et al, 2013).

Low carbon steel has been considered as one of the most important structural materials because of its stable chemical and good mechanical properties. It is mainly applied to the automobile, ship-making, and military industries due to its proper alloying concentrations that give this wide availability as our requirements and service grow (Pengyu et al, 2013). It is also widely applied to fabricate components in mining machinery, agriculture appliance, construction industry and foundry machinery for its desirable properties such as low cost, high strength, better harden ability and so on. However, these components would suffer fierce abrasive wear in service under sliding condition against the hard abrasive particles coming from rock, mineral, soil and slurry, which has caused enormous economic losses. So it is urgent and necessary to improve the abrasive corrosion resistance of these materials (Iordanova, 2008).

The main advantages of the surface treatment by high power lasers are connected with their high energy density, chemical cleanness, controllable temperature profile and locality of the processing (Khalid, 2011). During the laser treatment the materials are exposed to fast heating and cooling to ambient temperature, which usually causes surface melting and subsequent rapid solidification. (Shuja et al, 2013).

Recent work of the authors has demonstrated that LST of carbon steel with an excimer laser produced a relatively uniform melted layer, with a melt depth up to 20 μm; further, relatively
coarse intermetallic particles and dispersoids within the original alloy matrix were absent in the laser-melted region [Shuja et al, 2013; Knupfer et al, 2010].

The goal of this research is to produce a thick and integrated surface layer on the surface of a low carbon steel sheet by laser surface treatment (LST) using ND-YAG laser. Potentiostatic technique and Tafel tests were performed in order to study the corrosion behaviors of the untreated steel substrate and laser processed samples.

EXPERIMENTAL WORK

A sheet of low carbon steel with the chemical composition indicated in Table 1 was cut into specimens of dimensions of 2 cm x 2 cm x 0.4 cm. The surface of the alloy was polished up to the No. 1000 emery paper followed by 0.05 μm diamond paste, the specimens were carefully cleaned with water, rinsed with acetone and dried under air. Fig. (1a) shows the optical view for polished specimen while fig (1b) shows the microstructure for the specimen.

SURFACE TREATMENT BY LASER

An MED-810 model, pulsed Nd:YAG laser with laser wavelength 1064 nm was utilized for laser processing of the coated steel. The output pulsed beam was square in shape and in standard mode. The laser pulse frequency, pulse width, and pulse energy were 6 Hz, <10 ns and 1000 MJ, respectively. The treating area was 1 cm² and the space from the sample to the laser source was 9 cm. Figure 2 shows the specimen after laser treatment.

ELECTROCHEMICAL POLARIZATION

In order to investigate the corrosion resistance of the specimens, polarization tests were carried out in the range of -250 to 250 mV from corrosion potential. The rate of potential change was chosen to be 10 mV/min. The Potentiostat used in corrosion tests was MLAB 200. The corrosion rates were evaluated by Tafel test and the results were presented in mils per year (mpy). For all three specimens, the corrosion tests were performed in 1, 2, and 3.5 NaCl wt% solution and 25°C.

The polarization cell consists of working electrode (low carbon steel), reference electrode (Calomel) (the lugging probe was kept at distance of 1 mm from the surface of working electrode), and graphite rod (Auxiliary electrode), these electrodes were connected to a computerized potentiostat (Bank Electronics 200- German made).

HARDNESS TEST

The laser surface technique generated a self-quenching effect on the surface of steel and gave change in the microstructure. Due to it, the hardness of the steel surface was improved. It should be noted that laser can only harden the surface of a certain depth with pre-determined parameters such as energy and power density (Pengyu et al, 2013; Iordanova, 2008). The micro hardness of the specimens was measured before and after laser surface treatment by using (Digital Microhardness Tester HVS100) apparatus under a load of 100 g with effect time of 15 s. The values of hardness were averaged by at least five points of measurements.

RESULTS AND DISCUSSION

Figures 4, 5, 6, 7, 8, and 9 show the corrosion behavior for low carbon steel before and after laser surface treatment in 1, 2, and 3.5 % NaCl respectively.

The results show that the corrosion rates of the LST lower than that of the untreated carbon steel. In addition, laser surface treatment cause a considerable increase in the corrosion resistance of the steel compared to base specimen owing to the formation of passive layer represent corrosion resistant phases. The results of the Tafel tests in Table 2 also show a reasonable decrease in the corrosion rate of the carbon steel after LST process. According to Table 2, the corrosion resistance of the low carbon steel after treatment of laser surface increase many times.
Corrosion rate is calculated by using the equation (1).

\[
CR \text{ (mpy)} = \frac{0.13 \ I_{\text{corr}} \times \ E.W}{\rho} \quad \text{…(1)}
\]

where:
- \( I_{\text{corr}} \): corrosion current, \( \mu\text{A/cm}^2 \)
- E.W.: Equivalent weight of the specimen in g./ equivalent.
- \( \rho \): Density of specimen in g./ cm\(^3\).

Figures (3,4,5) and table (2) show the effect of NaCl concentration on carbon steel at room temperature before LST. The results indicate that increasing NaCl concentration increase the corrosion rate. This is due to the increasing in electrical conductivity of the solution due to increase in number of ions present. This is in agreement with many workers (Pengyu et al., 2013; Iordanova, 2008).

Figures (6,7,8) show the polarization curves of carbon steel after LST at room temperature with different NaCl concentrations. Increasing NaCl concentration increase the corrosion rate (table 2), as indicated above. Moreover the corrosion rates after LST are lower than that obtained before LST. this is due to the protective layer formed on the surface; this layer improves the corrosion resistance. The decrease in corrosion rate and the appearance of the protective layer can be explained due to the resolidification of metal surface in which the precipitates (alloying elements and impurities if exist) are dissolved and redistributed in oridinal alloying matrix according to the rapid melting and resolidification. Therefore the surface after LST is mostly free from alloying element; moreover more homogenous microstructure is obtained. The XRD test indicates that the surface after LST is more pure than that obtained before LST as shown in fig (11).

The above explanation is in agreement with many workers (Chong et al, 2013; Xin Tong et al, 2012; Shuja et al, 2013; and Knupfer et al, 2010). However the corrosion potentials of carbon steel move to more negative direction before and after LST with increasing NaCl concentration which indicate the cathodic reaction decrease with increasing NaCl concentration. This is because of lowering in \( O_2 \) concentration with increasing in salt concentration. Moreover after LST (1 and 2%) NaCl concentration, the corrosion potentials are more negative than that obtained before LST indicating that the desolving rate of carbon steel surface decrease by LST. At 3.5% NaCl concentration the corrosion potential moves to positive value with respect to corrosion potential before LST indicating that the anodic reaction is much less than that before LST due to the irradiation by laser technique, i.e the carbon steel surface is less corroded in sea water when treating with lasrer.

**AFM INVESTIGATION**

The roughness of surface film before and after L.S.T. process was determined by AFM as shown in table (3) and Fig. 9 and 10. The AFM image revealed that a rough film formed on the low carbon steel surface after L.S.T., and it is increases compare with that of the polish surface. This is due to the new layer created on the surface because of fast melting and resolidification. The types of this layer appear as spherical or semi-spherical.

**HARDNESS TEST**

The Vickers micro-hardness testing results are listed in Table (4).

Comparing the results with the hardness of low carbon steel before LST (130 HV) and that obtained after LST, it’s clearly shown that the hardness of LST surface is greater than untreated surface. The increased surface hardness is due to continued carbon dissolution from the pearlite and the local minimum is associated with recrystallization. This comes in good agreement with (Knupfer et al,2010; Abdolahi et al,2011; Shin et al,2007) as he has studied the effects of laser forming on the mechanical and metallurgical properties of low carbon steel, and found greater hardness in comparison with the untreated alloy.
CONCLUSION
The following conclusions can be drawn from this study:

1- The laser surface treatment improve the corrosion resistance of low carbon steel in different concentrations of salt solution due to the fast melting and resolidification of metal surface.
2- The roughness and hardness of low carbon steel increases after LST.
3- The surface of low carbon steel is more pure than that obtained before LST as shown by XRD analysis.

Acknowledgments
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REFERENCES


4- Pengyu Lin , ZhihuiZhang , HongZhou , LuquanRen, (2013)," The mechanical properties of medium carbon steel processed by a biomimetic laser technique", Elsevier publisher, Materials Science & Engineering,A 560, 627–632


Table (1) Standard and analytical chemical compositions of low carbon steel alloy

<table>
<thead>
<tr>
<th>Metals</th>
<th>Iron</th>
<th>Carbon</th>
<th>Manganese</th>
<th>Aluminum</th>
<th>Copper</th>
<th>Sulfur</th>
<th>Phosphorus</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard by</td>
<td>Rem.</td>
<td>0.02-0.06</td>
<td>0.35 max</td>
<td>-</td>
<td>-</td>
<td>0.035 max</td>
<td>0.030 max</td>
</tr>
<tr>
<td>ASTM A568</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Analysis by</td>
<td>99.6</td>
<td>0.04</td>
<td>0.16</td>
<td>0.03</td>
<td>0.02</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(wt.%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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Table (2) Corrosion rate of low carbon steel before and after L.S.T

<table>
<thead>
<tr>
<th>Carbon steel specimens</th>
<th>NaCl Conc. wt %</th>
<th>$E_{corr}$ mv</th>
<th>$I_{corr}$ $\mu$A/ cm$^2$</th>
<th>C.R. MPY</th>
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<tr>
<td>Before L.S.T</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>-338.9</td>
<td>1.10</td>
<td>0.238</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>-348</td>
<td>2.49</td>
<td>0.539</td>
<td></td>
</tr>
<tr>
<td>3.5</td>
<td>-539.5</td>
<td>15.19</td>
<td>3.287</td>
<td></td>
</tr>
<tr>
<td>After L.S.T</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>-379.7</td>
<td>0.578</td>
<td>0.125</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>-390.5</td>
<td>0.715</td>
<td>0.155</td>
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<tr>
<td>3.5</td>
<td>-450.8</td>
<td>2.93</td>
<td>0.634</td>
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</table>

Table (3) Roughness of low carbon steel before and after L.S.T

<table>
<thead>
<tr>
<th></th>
<th>Before L.S.T</th>
<th>After L.S.T</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.85</td>
<td>2.54</td>
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</table>

Table (4) Vickers micro-hardness (a) before LST (b) after LST

(a)

<table>
<thead>
<tr>
<th>Test No.</th>
<th>HV</th>
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<tbody>
<tr>
<td>1</td>
<td>129</td>
</tr>
<tr>
<td>2</td>
<td>134</td>
</tr>
<tr>
<td>3</td>
<td>131</td>
</tr>
<tr>
<td>4</td>
<td>128</td>
</tr>
<tr>
<td>5</td>
<td>130</td>
</tr>
<tr>
<td>Ave.</td>
<td>130</td>
</tr>
</tbody>
</table>

(b)

<table>
<thead>
<tr>
<th>Test No.</th>
<th>HV</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>170</td>
</tr>
<tr>
<td>2</td>
<td>188</td>
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<tr>
<td>3</td>
<td>165</td>
</tr>
<tr>
<td>4</td>
<td>190</td>
</tr>
<tr>
<td>5</td>
<td>175</td>
</tr>
<tr>
<td>Ave.</td>
<td>177</td>
</tr>
</tbody>
</table>
Fig (1) Microstructure of carbon steel  
(a) after polishing  
(b) after etching

X 250

Fig 2 microstructure for carbon steel after laser surface treatment.

X 750

Fig (3) polarization curve for low carbon steel before LST at 25°C and 1%NaCl
Fig (4) polarization curve for low carbon steel before LST at 25°C and 2% NaCl

Fig (5) polarization curve for low carbon steel before LST at 25°C and 3.5% NaCl
Fig (6) Polarization curve for low carbon steel after laser surface treatment at 25°C and 1% NaCl solution

Fig (7) Polarization curve for low carbon steel after laser surface treatment at 25°C and 2% NaCl solution
Fig (8) Polarization curve for low carbon steel after laser surface treatment at 25oC and 3.5 % NaCl solution

Fig. (9) AFM Surface scans of polish surface low carbon steel
   a. (3D) View.
   b. (2D)View. Section analysis showing roughness parameters
Fig. (10) AFM Surface scan of low carbon steel after laser surface treatment (3D) View.
(2D) View. Section analysis showing roughness parameters

Fig (11) XRD test for low carbon steel: (a) before LST, (b) after LST.