ANALYSIS OF THE EFFECT OF SURFACE OXIDATION ON THE LASER TRANSFORMATION HARDENING OF CR-MO STEELS

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Abstract

Laser surface hardening is a technology that enables important advantages to be obtained in comparison with conventional techniques in terms of accuracy of the heat affected zone and productivity. Nevertheless, the development of realistic and flexible models has to be fulfilled in order to control the effects of every set of process conditions. Despite many different models having been developed, very few of them deal with the increment of absorption related with the instantaneous value of the layer of oxide growth during the process in a non-protective atmosphere. This work analyzes, on one hand, the problem of oxide formation at the external surface using kinetic relations, whose parameters have been related with the process variables, considering non-equilibrium conditions. Then, the oxide thickness was associated with a value of absorption through an innovative formula that considers the path of the laser radiation in the interface oxide-base material. On the other hand, when the dimensions of the surface to be treated are larger than the cross section of the laser beam several overlapped tracks are needed, and the distance between consecutive tracks becomes a fundamental design parameter. This work aims to optimize such parameter with the purpose of fulfilling a set of initial requirements avoiding the softening of the martensite achieved in the previous track. The model, in conjunction with a convenient geometrical characterization of the heat affected zone, enables a design strategy to be implemented which, using metallurgical and hardness maps, has the capability of attending different criteria. All the conditions proposed in the design of a suitable overlapping distance have been reproduced empirically for the case of the 42CrMo4 steel.

Keywords: Laser-Hardening; Annealing; Martensite; Oxidation; Steel
1. Introduction

Laser surface hardening is an innovative technology to increase the hardness and wear resistance for industrial parts undergoing cyclical loads and/or friction. This process has the potential to offer high standards of quality and accuracy of the heat affected zone in comparison with conventional techniques.

In the laser surface hardening process martensite is obtained by a laser beam, with relatively high energy density, that traverses the surface of a steel part causing a very quick heating (between $1000\, K/s$ and $6000\, K/s$), followed by another quick self-quenching of the material. The typical scope of the treatment lies between 1 mm and 3 mm, and it is limited by the possibility of having adequate thermal cycles beyond these positions without melting the surface.

One of the collateral consequences of the process is the oxidation of the treated surfaces, [1, 2]. The high temperature reached during the process, (between 900 °C and 1400 °C), accelerates the kinetic of the chemical reaction between the steel and the surrounding air, leading to the formation of a layer mainly composed by Fe$_3$O$_4$ [3, 4]. This layer increments the absorption of the laser radiation up to 40 % from the original conditions.

Given this significant increment, it is essential to introduce a realistic approach of the phenomena in the development of any thermal and metallurgical model of the process.

Another important characteristic of the laser surface hardening is fast austenization. The heating rate produced by a moving laser source is comparable in order of magnitude with the time taken by the carbon atoms to diffuse inside the base material to form austenite. The higher the heating rate the higher final austenization temperature results [5], and therefore, equilibrium critical temperature, $Ac_3$, only means an energy threshold from which the reaction is thermodynamically possible [6], but not a reliable reference to ensure complete phase change from the base material into austenite.

The present work, firstly, deals with the kinetic of the oxidation reaction when a laser is irradiating the surface. It proposes the determination of the oxide layer coupled with the thermal courses, using a kinetic law, whose parameters have been functionally related with some process parameters characteristic of the laser surface hardening, enabling a flexible model to face a wide range of process conditions. Once the instantaneous thickness can be calculated, the next step is to associate it with another instantaneous increment of absorption. An innovative formula deduced from the path followed by the radiation in the interface oxide-base material will be put forward.

In the second place, the accurate thermal courses calculated through the thermal-oxidation coupling will be analyzed with Avrami law to calculate the fraction of austenite resulting from the process. This procedure will be done in a way similar to what [7] proposes, although, using real thermal cycles, with non constant heating and cooling rates.

Despite involving a certain computational effort, because the thermal courses have to be discretized into almost-isothermal steps, the effort is significantly lower than having to design and solve a network representing the microstructure of the base material, and the availability of the model to calculate realistic geometries and long duration processes is ensured.

2. Material and experimental procedure

The AISI 4140 (EN 42CrMo4) steel in a quenched and tempered state has been selected as working material.

The geometry of the investigated component corresponds to cylindrical rods with diameter 68 mm and width 20 mm (whose size has been taken from the real dimensions of the rod journals of the crankshaft from a conventional automotive engine). A 30 mm diameter axis has been fixed concentrically with the rod allowing it to be animated with uniform circular movement. Fig.1 displays a scheme of the process. The most important user-controlled parameters are the process velocity, $V_p$, as a product of the sample radius, $R$, by the angular velocity of the rod, $\omega$; the offset between the axis of the laser beam and the vertical axis at the center of the rod measured within the plane that contains both of them, $Off$, and the characteristics of the laser beam itself: beam size, power, $P$, spatial distribution or irradiance, $I$ and wavelength, $\lambda$. Considering the offset as a process parameter enables the effect of changing both, the projected area of the beam over the surface and the incidence angle, to be studied, broadening the flexibility of the process.

Fig. 1 shows a schematic representation of the process setup, considering the cylindrical geometry of the treated sample.
The laser source is a high power diode laser delivering radiation at wavelength of $\lambda=900 \pm 10$ nm.

All the samples have been cut using an Al$_2$O$_3$ wheel, then ground, and finally conveniently polished. Nital (2% nitric acid and 98% ethanol) was used in order to etch the samples. The microstructure characterization has been carried out by an optical microscopy looking for an accurate measurement of the depth and width of the transformed zone. In order to have an estimation of the oxide layer after the process, it has been additionally checked using a thickness measurer, model TEC-CM20 from Tecnumetal, capable of detecting the layer of a non-conducting material over the surface of a conducting one (impedance analysis).

3. Theoretical modeling

Fig. 2 shows a scheme of the model. The high temperature reached during the process under a non-protective atmosphere leads unavoidably to the oxidation of the iron present in the surface of the part, developing a layer mainly constituted by Fe$_3$O$_4$, [3, 4].

The growth of the oxide layer while the laser beam irradiates any region of the surface increases the amount of energy absorbed into the material due to the increment in the roughness of it. Although it is a widely accepted phenomenon and many authors deal with it [1, 3, 4], few of them study the way in which the laser, as a high density energy source producing a very fast heating, moves the reaction far away from the equilibrium. [2], nevertheless, shows the dependence of the kinetic parameters on the Arrhenius equation, activation energy, $E_A$, and the pre-exponential term usually referred as frequency factor, $F_F$, with the temperature reached as a result of a laser heating, observing changes of even several magnitude orders depending on it. This work proposes the calculation of the thickness of the oxide layer, $y$, using a kinetic law whose parameters, $E_A$, and $F_F$, are dependent on the process characteristics. Then, the instantaneous thickness will be related, at every step of the calculation, with the corresponding rise of absorption using an innovative formula based on theoretical considerations. This approach enables a dynamic feedback between the absorption due to the oxidation and the thermal courses to be implemented onto the model, differing from the use of a unique constant value to consider the oxidation, as is typically done.

According to [7], most of the oxidation phenomena follow a kinetic law linear type, parabolic type, logarithmic type, or asymptotic type.

The linear modeling, would imply that the growing speed of the layer is constant, or, in other words, that a specific thickness of it does not affect the developing of further thicknesses. It would be only possible if the layer disappears immediately after its creation. This behavior is not observed in a hardening process.

The asymptotic law, assumes that the oxide layer is limited to a maximum thickness, which means that, it is capable of isolating completely the base material and stopping the reaction. The high thermal gradients during the process and the porous structure of the layer indicate that this hypothesis is not possible either.

The logarithmic law, according to [7], is predominant at relatively low temperature, around 200 °C, given the low ionic conductivity at that temperature. Nevertheless, the conditions of the laser hardening imply much higher temperatures. Therefore, the most appropriate law to characterize the growing of the oxide layer on a laser hardening process is the parabolic law, eq. (1).

$$y = \sqrt{K_p \cdot t}$$  \hspace{1cm} (1)

The kinetic constant of the parabolic law, $K_p$, is given by eq. (2).
\[ K_p = F_f \cdot \exp(-E_a / RT) / \rho^2 \]  \hspace{1cm} (2)

\( R \), represents the gas constant and \( \rho \), the density of the oxide, introduced to express the oxide layer directly in length units.

The activation energy can be described as the threshold barrier that has to be surpassed to start a chemical reaction. While in non-catalyzed reactions it is regarded as a constant value [8], the very fast continuous heating imposed by the laser during the hardening process competes with the time taken for the reaction between the activation energy having been reached and it starts properly, that, we will call \textit{initiation} of the chemical reaction. Although the time consumed by the initiation normally can be neglected, the very high heating rate caused by the laser, will make the temperature keep rising while initiation is taking place, resulting in a start of the chemical reaction at a higher temperature than if it happens with a slower heating rate. As a consequence of this process, the higher the heating rate is the higher the apparent activation energy results, according to the final temperature in which the reaction starts. This enables the activation energy to be considered as a function of the heating rate, eq. (3).

\[ E_a = \varphi \frac{dT}{dt} \]  \hspace{1cm} (3)

The frequency factor quantifies the number of collisions between the molecules of the reagent [10]. Once the reaction has started, and the activation energy has been surpassed, the frequency factor determines the growing rate of the oxide layer. Again the presence of a high density source of energy such as a laser beam over the area where the chemical reaction is taking place stimulates the pace of collisions, and therefore, the frequency factor has to be functionally related with the irradiance of the laser after the start of it. Nevertheless, similar values of irradiance over the surface may be acting on reactions that might have been initiated with very different activation energies.

Fig. 3 displays the longitudinal section of two hypothetical beams where their frontal side is different, leading to a more progressive heating on the left, and a more abrupt one on the right, but, whose rear regions are completely equal. The arrow represents the direction of their movement.

According to eq. (3) the activation energies for the beams of fig. 4 have been different, and, although, once the reaction has started is going to be stimulated by the same level of irradiance, the effect of the different conditions at the start has to be taken into account. Consequently, the frequency factor has to be functionally related not only with the irradiance of the beam, but also with the apparent activation energy that the process conditions have imposed to the reaction, eq. (4).

\[ F_f = \varphi \left[ I(t), E_a \right] \]  \hspace{1cm} (4)

The aim of an accurate determination of the oxide layer is to use this information to calculate the increment of absorption associated with the state of the surface. When the base material remains unoxidized and the roughness of the surface is considered negligible, the amount of energy absorbed by the material is given by the so-called Fresnel equations.

If the oxide layer appears, part of the energy initially reflected from the base material, that can be called \textit{Fresnel Reflection}, \( R_F \), (equal to \( 1-A_F \), \textit{Fresnel Absorption}.), will again be reoriented against the surface of the material, repeating the process: some of the redirected radiation will be absorbed, and part again sent to the oxide layer. This sequence is repeated until the energy has been completely absorbed or released from the material; Fig. 4.

Mathematically, the total energy absorbed by the base material, \( A_F \), can be considered the sum of the energy absorbed in every single impact of the
radiation, compound of the energy reflected in the previous impact that has been efficiently redirected by the oxide layer. The efficiency of the oxide layer to redirect the radiation against the material, is denoted by $\mu_{Ox}$, and will depend on the thickness of the oxide layer at every moment, Eq. (5).

$$A_T = A_F \left[ 1 - R_F \cdot \mu(y)_{Ox} \right]$$

(5)

In eq. (1), if $\mu_{Ox}$ is considered directly proportional to the thickness of oxide, $y$, then $A_T$ will show an asymptotic behavior tending to a value of 1, coherent with the fact that absorption has to be limited to 100% no matter how much the thickness surpasses a certain value.

While the oxide layer has not appeared, $y=0$, the value of $A_T$ matches the absorption coming from Fresnel equations.

In the time from when a given amount of energy has reached the part until it has been completely absorbed or released, the thickness of the oxide layer can be assumed constant, since the speed of light is much faster than the development of the chemical reaction.

Different from the works where the oxidation is characterized by a global absorption coefficient or with an increment of absorption dependent of the thickness, Eq. (5) introduces the idea of “redirecting efficiency”, $\mu_{Ox}$, which will lead to different final values of absorption according to the energy initially reflected by the surface, $R_F$.

4. Results and discussion

The characterization of the kinetic parameters has been carried out through a successive procedure, which, starting with parameters of reactions close to the equilibrium taken from [10, 11], have been modified, coherently with the established hypothesis, until achieving results in the model matching the experimental temperatures, and, predicted oxide layers similar to the measurements. As is apparent from this argument, if the thermal courses were used for the adjustment procedure, the increment of absorption due to the oxide had to be taken into account at the same time. Therefore, the kinetic parameters were needed to be determined after a reasonable estimation of the redirecting efficiency of the oxide for different thicknesses.

The values of the maximum absorption reported by [1,12], in the range of 60%-73%, depending on the process parameters, along with our own measurements of the oxide thickness, between 5 $\mu$m and 30 $\mu$m, enables the relation, $\mu_{Ox}(y)$, to be constructed.

Table 1 synthesizes different process conditions tested and the resulting kinetic parameters.

<table>
<thead>
<tr>
<th>$V_p$ (mm/min)</th>
<th>$P$ (W)</th>
<th>Off (mm)</th>
<th>$T_{Max}$ (°C)</th>
<th>$Ea$ (J/mol)</th>
<th>$F_f$ (Kg²/m⁴s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>250</td>
<td>305</td>
<td>0</td>
<td>136</td>
<td>21000</td>
<td>150</td>
</tr>
<tr>
<td>400</td>
<td>340</td>
<td>0</td>
<td>115</td>
<td>21700</td>
<td>550</td>
</tr>
<tr>
<td>600</td>
<td>400</td>
<td>0</td>
<td>137</td>
<td>22000</td>
<td>60000</td>
</tr>
<tr>
<td>1000</td>
<td>493</td>
<td>0</td>
<td>125</td>
<td>22500</td>
<td>90000</td>
</tr>
</tbody>
</table>

From the experimental results $Ea$ is expressed through an explicit expression, eq. (6):

$$E_a = -4.188 \cdot 10^8 \cdot (dl / dt)^{-138} + 230582$$

(6)

In eq. (6), the magnitude $dl/dt$ has to be expressed in W/cm²s. Its asymptotic behavior shows that the effect of increasing the suddenness of the heating tends to have a limited effect on the activation energy from a certain value. Despite the proposed equation having an asymptote close to 220600 J/mol, it has to be interpreted as a trend in the not very quickly growing behavior of the function, more than as a fixed value.

In the same way, $F_f$, is fitted, according to the hypothesis set in eq. (4), using a polynomial equation, with grade 2 for the irradiance and 1 for the activation energy, eq. (7).

$$F_f = 96170 + 134900 \cdot E_a - 113500 \cdot I$$

$$-140700 \cdot E_a \cdot I + 4270 \cdot I^2$$

(7)

Eq. (7) requires $I$ to be introduced in W/cm² and $Ea$ in J/mol.

Eqs. (6) and (7) have been planned from theoretical considerations, and adjusted empirically. A comprehensive understanding of the activation energy under very high heating rates has to be accomplished, including the influence of the heating rate over the initiation of the chemical reaction and other nonlinearities; additionally, the interpretation of the resulting mathematical functions and the coefficients from the adjusting process need to be deeply understood and particular situations taken into account in future...
works. However, the process conditions used to prepare the functions cover most of the laser surface heating possibilities, and lead to satisfactory results that will be shown in the successive sections.

Table 2 synthesizes the characteristics of the experimental tests and the maximum temperature measured.

<table>
<thead>
<tr>
<th></th>
<th>P (W)</th>
<th>( V_p ) (mm/min)</th>
<th>Off (mm)</th>
<th>( T_{\text{Max Exp.}} ) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Test 1</td>
<td>2070</td>
<td>200</td>
<td>21</td>
<td>1233</td>
</tr>
<tr>
<td>Test 2</td>
<td>3750</td>
<td>600</td>
<td>27</td>
<td>1250</td>
</tr>
<tr>
<td>Test 3</td>
<td>4300</td>
<td>500</td>
<td>31</td>
<td>1150</td>
</tr>
</tbody>
</table>

Fig. 5 displays the thermal courses provided by the model for Test 1 whose values are indicated on the left vertical axis, and the development of the oxide layer, that is referred to on the right horizontal axis. Z represents the depth under the surface for the thermal cycles.

As it corresponds to a relatively slow process, the interaction time (time during which temperature remains above the equilibrium critical temperature), is considerable for the points around 1.5 mm. The maximum temperature predicted by the calculations is 1239 °C, that presents very slight differences with the experimental result (see Table 2).

The growth of the oxide layer shows certain correspondence with the thermal cycles. The final value, around 20 μm, lies within the expected magnitude order.

Fig. 6 represents the comparison between the austenitic fraction predicted by the calculations and the heat affected zone revealed by the chemical etching of the treated sample.

Numerical calculations are able to predict the depth of the affected zone and the general shape of it, although some irregularities can be appreciated as a consequence of the graphical interpolation of the calculated values, the general shape is satisfactory.

Fig. 7 displays the thermal courses and the oxide layer corresponding to Test 2.

As it corresponds to a faster process the interaction time has been drastically reduced in comparison with Test 1, partially compensated with a larger value of Off. The correlation between the oxide layer development and the thermal course for Z=0, compared with Test 1, shows a starting of the oxidation at a higher temperature in the case of Test 2, given the higher suddenness of the heating (for the same spatial distribution of the laser beam, \( V_p \) is threefold and P almost twofold). In addition, the slope of the growing of the oxide layer is also bigger as a consequence of the higher levels of irradiance associated with a higher power.

Fig. 8 shows the comparison between the experimental and the predicted transformation zone for Test 2.

Fig. 8 shows a good correspondence between the calculated and the experimental heat affected zone, for both depth and general shape. In comparison with Test 1, the maximum depth is shorter as corresponds to a faster process.
Fig. 9 represents the thermal cycles and the oxide layer associated with Test 3.

![Figure 9: Thermal cycles and oxide layer of Test 3](image-url)

Maximum temperature of 1160 °C practically matches the empirical result and the oxide layer happens to be the most reduced of the three as it corresponds to a fast process in which the maximum temperature is lower than in the others.

Fig. 10 shows the austenization map corresponding to Test 3.

![Figure 10: Heat affected zone vs. calculated for Test 3](image-url)

Fig. 10 demonstrates again that the method allows a good agreement between calculations and experimental results. In this case, maximum depth lies around 1.2 mm, which is coherent with the conditions of the process, and the lower temperature reached in comparison with both the others.

5. Conclusions

The main and most innovative characteristics of the model and the major results are synthesized as follows:

a) A coupled temperature-oxidation 3D model including the relation of the kinetic parameters characterizing the oxidation with the features of the process has been developed. This improves the flexibility of the model to deal with very different process conditions considering the oxidation phenomenon associated to every single one.

b) The calculations of the increment of absorption as a consequence of the development of the oxide layer, for every stage of it during its growth have been included.

c) The feedback of the thermal calculations with the absorption due to every stage of the oxide layer has led to very accurate results in the comparison between the real and calculated maximum temperature with a relative error within 5% in all the cases.

d) The model is able to offer the temporal course of the oxide thickness, which, in every test has fallen between the margins experimentally determined. These results have been checked through the measurement of the experimental oxide layer.

e) The transformation profile using Avrami law with discretized almost- isothermal steps, has been obtained showing a good agreement between theoretical and experimental results.

f) The resulting model has shown its capability to face different process conditions and domains, allowing a wide range of situations to be considered, particularly, those which imply changes in the heating rate or in the interaction time.

Some tasks and further studies are needed to deepen the understanding of the phenomena happening during laser surface hardening:

g) The influence of the process variables included in eqs. (20) and (21) and the non-equilibrium reaction described by them need additional studies to understand completely the nature of the phenomenon.

h) Despite the oxide layer having been measured indirectly through impedance analysis, an optical characterization to analyze its compactness and the trail of possible release of material during the irradiation, would add interesting complementary information.

i) A further characterization of the products from the cooling of the formed austenite, to develop not only a comparison between austenite profile and heat affected zone but also an accurate study of all the products obtained during cooling and the concentration of everyone.
6. Acknowledgements

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References


