A Study on the Enhancement of Chemical and Mechanical Properties of Low Carbon Steel Surface Cleaned with a Nanosecond Pulsed Laser

Vishnu Narayanan, Almigdad W.G. Ali, Ramesh Singh, and Deepak Marla*

Department of Mechanical Engineering, Indian Institute of Technology Bombay, Mumbai, INDIA
**Corresponding author's e-mail:* dmarla@iitb.ac.in

Laser cleaning has been observed to alter the surface properties of steel surfaces. The change in surface properties is greatly affected by the laser parameters and therefore, the selection of appropriate laser parameters is paramount. In this work, a study on the treatment combination of laser power, scan speed, pulse repetition rate, and hatch distance on the surface hardness and the mass percentage of iron is conducted via response surface methodology using a central composite design. The factors and interactions that significantly affect the response were identified by analysis of variance (ANOVA). The microhardness was measured using a Vickers hardness testing machine and the mass percentage of iron was obtained by energy dispersive x-ray spectroscopy (EDS) analysis. The hardness value was observed to remain almost unchanged or increase by more than 200 % and steel was completely reduced to even 100 % pure iron at different laser parameters. The responses were approximated by a second-order regression model and the R-squared values for the models of hardness and mass percentage of iron are 84 % and 80 % respectively. The model can be used to predict the parameters that result in the desired surface hardness and iron content during cleaning.
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1. Introduction

Laser cleaning is emerging as a very popular industrial application due to its numerous advantages [1]. One of the main applications is the precise removal of corrosion layers. Removal of the corrosion layer with pulsed lasers has been reported to alter the surface properties of steel surfaces [2]. Many studies have reported the enhancement of surface properties after laser cleaning of the oxide layer from steel [1-5]. The change in surface properties is affected greatly by the laser parameters used for cleaning and therefore, the selection of appropriate laser parameters is paramount. A deep understanding of the interaction effect is important in the selection of laser parameters for laser cleaning and surface enhancement processes. Many studies have been conducted to understand the effects of various laser parameters on the cleaning efficacy and surface properties after cleaning rusted steel surfaces.

The effectiveness of laser cleaning on the removal of paint from steel surfaces and the surface properties after cleaning were studied by Li et al [2]. A detailed study on the impact of parameters like laser power and scan speed on the laser cleaning of rust layer on steel was done by Wang et al. [1]. The study contained a detailed investigation of the individual effects of laser fluence and scan speed on cleaning efficiency. The study also included the effect of laser parameters on the roughness of the cleaned surface and the effect of laser fluence on surface hardness and corrosion resistance. Ma et al. investigated the surface integrity of steel after oxidation removal by a nanosecond pulsed laser [4]. The individual effects of variation of power, overlap and pulse repetition rate (PRR) on the elemental composition and surface hardness were studied. The corrosion resistance of the laser-cleaned surface was also studied. A similar study on the effect of surface parameters on surface finish and corrosion resistance during CW laser cleaning was conducted by Zhuang et al. [5]. The effect of laser cleaning parameters on the surface chemistry, microstructure and mechanical properties of corroded stainless steel surfaces was studied by Yoo et al. [6]. This study focused on the change in surface chemistry and mechanical properties at different laser scanning parameters and overlaps. Laser cleaning using ill-judged parameters is known to cause steel surfaces to become dark and discoloured as reported by Narayanan et al [7]. Zhang et al [8] conducted a study on a laser cleaning procedure consisting of two scans, where the first scan removes the corrosion layer and the second scan removes the oxide layer formed due to the first scan without causing any further oxidation. The appropriate parameter values for both scans were numerically predicted by a laser heating model. The results of these studies elucidated the change in chemical and physical properties of the corroded steel surfaces that were cleaned with laser. Among the changes observed, the increase in surface hardness and surface oxidation is of great practical significance. Surface hardness directly affects the usability of the surface for several applications where wear resistance is important. Surface oxidation on the other hand has a complex relationship with the appearance as well as the corrosion resistance of the laser-cleaned surface.

Though many studies have reported the effect of laser parameters on the chemical and mechanical properties, no studies were found that applied a treatment combination to investigate the interaction effect of different factors. The comprehension of the interaction effects of the different parameters would help us predict laser parameters that result in desirable surface properties after cleaning with a single scan. In this study, the effect of four laser parameters (laser power, scan speed, pulse repetition rate, and hatch distance) and their interaction on the surface hardness and the mass percentage of iron on the surface is investigated. The micro-hardness was measured using a Vickers hardness testing machine and the mass percentage of iron was obtained by energy dispersive x-ray spectroscopy (EDS) analysis. The work demonstrates the significance of the interaction effects on the surface hardness and iron content of a laser-cleaned steel surface. This model is useful in determining the laser parameters that would ensure maximum surface hardness and optimum iron content. The study demonstrates that there exists a window of parameter values that results in a surface with high surface hardness, shiny appearance and low oxide content with a single scan.

2. Experimental Set-up

In this study, naturally rusted AISI 1018 steel samples were used. The samples used in the study were naturally rusted samples with a thin rust layer (thickness < 20 µm). To reduce the effect of macro roughness of the surface during laser cleaning, the samples were flattened and lapped to a surface roughness of ~ 200 nm before it was exposed to the environment for corrosion. The unevenness rust and roughness of the rust layer due to the natural rusting process was reduced significantly due to this.

. Figure 1 shows a schematic of the experimental setup used for the study. The experimental set-up consists of a fiber laser (Model: MFP-30W-NABBA4.0) with a wavelength of 1060 nm, a pulse width of 100 ns, and a beam diameter of 9 mm. The laser beam is delivered through an optical fiber to a galvo-scanner equipped with an f-theta lens which focuses the beam to a spot diameter of 40 µm. The workpiece is placed horizontally on an x-y stage at the focal distance of the lens. The experiments are conducted by varying laser power in the range of 7.5-30 W and PRR in the range of 20-80 kHz. The laser beam is scanned at speeds in the range of 250-1500 mm/s. Laser cleaning is carried out by scanning parallel straight lines with a fixed distance (hatch distance, h_d) between each other. This hatch distance was varied in the range of 10-50 µm. The range of parameters was chosen such that there would be complete cleaning at all thickness and roughness values. Therefore, the results can be considered valid for thin naturally rusted materials with inherent roughness and variable thickness as the effect of both these have been accounted for in the study.

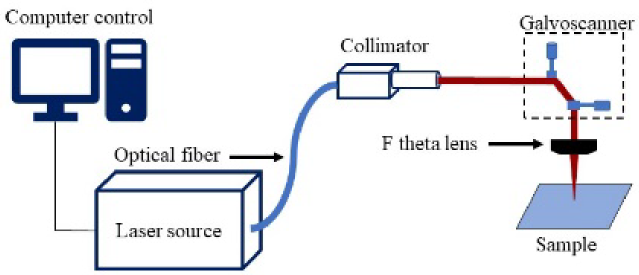

Fig. 1 Schematic of laser set-up used for the experiments.

3. Methodology

The objective of the study is to understand the effects of four different laser parameters on the appearance, chemical composition and hardness at the surface. The surface after cleaning is visually inspected using Alicona infinitefocus. The chemical composition of the surface is quantified using X-ray energy-dispersive spectroscopy (EDS) in OXFORD Instruments (make X-Max^N). The surface hardness is measured using a Vickers microhardness tester. The study on treatment combination is conducted via response surface methodology using a central composite design. The factors and interactions that significantly affect the response were also identified by using analysis of variance (ANOVA) modelling. The analysis provides us with the p values and F values of the terms of the linear model from which the insignificant terms could be identified. A reduced model is then obtained by removing the insignificant terms. In this work, a 31-run central composite design (CCD) model is used to study the behaviour of the responses, Vickers hardness (H) and iron content with four factors (power, scan speed, PRR, h_d) at five levels. The CCD analysis was conducted with 5 readings per design point to account for the repeatability of the experiments. Multivariate regressions were used to fit the following second-order polynomial model to the data from CCD, as given by,

$$f(x) = \beta_0 + \sum_{i=1}^{4} \beta_i x_i + \sum_{i=1}^{4} \sum_{j=1}^{4} \beta_{ij} x_i\, x_j + \sum_{i=1}^{4} \beta_{ii} x_i^2, \quad (1)$$

where $f(x)$ is the response, β_i is the ith coefficient of the regression equation, and x_i is the ith factor. A wide range of parameters is available due to the large number of commercially available lasers. The range of parameters considered in this study is a relatively small region compared to the range of laser parameters available. A second-order polynomial model can give a reasonable approximation of the true functional relationship over a small range of parameters. Table 1 shows the levels of different factors used in the CCD study.

Table 1 Levels of factors for CCD analysis.

Factors	-2	-1	0	1	2
Power (W)	7.5	13.1	18.75	24.4	30
Speed (mm/s)	250	563	875	1188	1500
PRR (kHz)	20	35	50	65	80
h_d (µm)	10	20	30	40	50

The significance of any regression model in predicting the effects of a set of independent variables on response variables is evaluated by conducting the F-value test. It is a probability distribution test and it is used to compare the variance by examining the ratio of the square to the appropriate residual error of the mean model [9].

4. Results

4.1 Appearance of the material

Figure 2 shows the surface of a rusted steel sample after 31 experimental runs. There is a clear difference in the appearance of the surface after laser cleaning with different parameter values. A few experimental points are observed to have a shiny appearance post-laser cleaning (as shown in the green box). This shiny appearance or metallic lustre is considered an indicator of the cleanness of metals and alloys and is closely related to the aesthetic appeal of metal parts. On the other hand, some experimental points were discoloured after the cleaning operation (as shown in the red box). The creation of a shiny surface is the desired outcome of the laser cleaning process. The change in colour during laser processing is related to the formation of oxides on the surface. The chemical composition of the regions under green and red boxes in Fig 2 was analysed using EDX. Figure 3 shows the enlarged image of the region and the area map of elemental oxygen. The concentration of green coloured dots in the image represents the relative concentration of elemental oxygen on the surface. The Fe and O content across a section AA' that was taken through the shiny region, rusted region

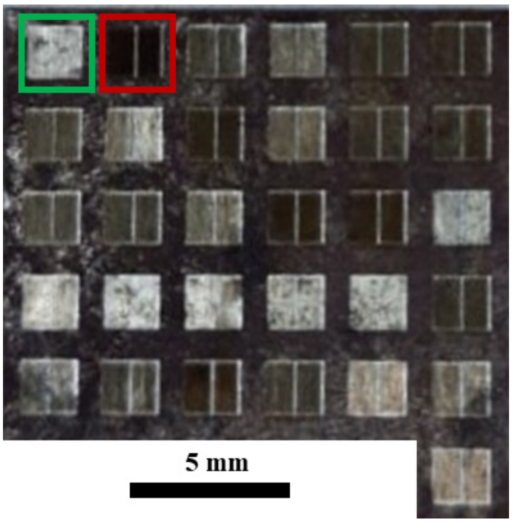

Fig. 2 Surface after 31 runs of rust cleaning experiments.

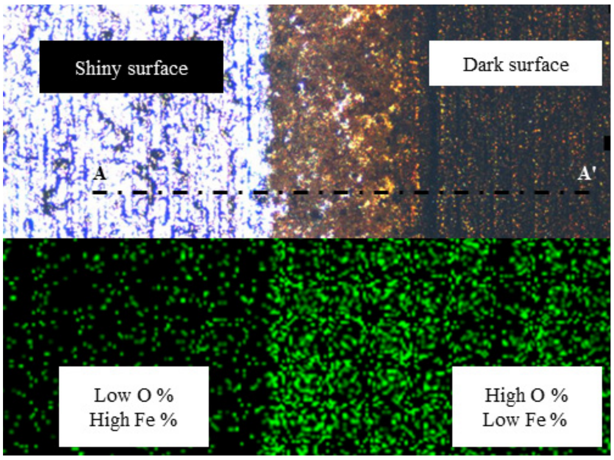

Fig. 3 Area mapping of oxygen content in shiny and dark surfaces created during laser cleaning.

and dark region is shown in Fig 4. The analysis showed that the shiny surface has a lower oxygen content and higher Fe content. The darkened region on the other hand had a much higher oxygen content and lower iron content compared to the shiny region. The higher oxygen content may be due to re-oxidation of the surface. Laser cleaning of the surface causes intense localized heating on the surface of the material. Depending on the laser parameters the heating and cooling rates would differ. When the surface is maintained at a high temperature it becomes vulnerable to oxidation and the oxidation leads to darkening. To avoid this, the laser parameters that lead to lesser oxidation have to be identified. The investigation of oxidation is explained in the following section.

4.2 Chemical composition of the surface

Oxide layers formed during laser cleaning operations of the 31 experimental runs were studied using EDX. The relative oxygen content was qualitatively studied using the Fe content (M_{Fe}) since EDX analysis is generally more accurate for elements with higher atomic numbers. The surface with higher Fe content will have a lower O content. The scanning of steel surfaces using nanosecond pulsed lasers causes the formation of a comparatively large melt pool and HAZ on

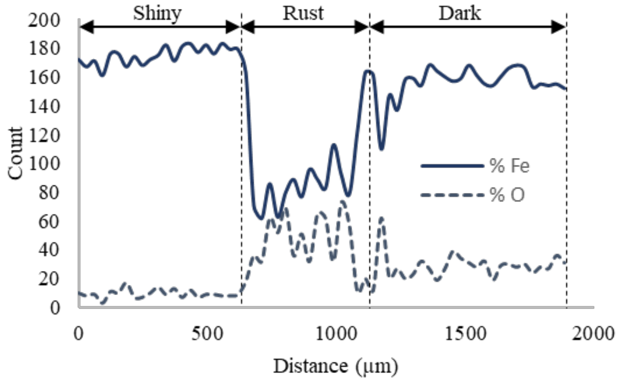

Fig. 4 Elemental composition of FE and O along section AA'.

the surface [10]. Steel surfaces are naturally vulnerable to corrosion and high temperatures increase the reaction rates of oxidation reaction. High powers, high overlaps and low scan speeds lead to a higher energy deposition on a localized area. This causes the surface to remain at higher temperatures for longer periods, increasing the amount of oxidation and thereby darkening the surface. The effect of the oxidation can be understood by the final iron content of the surface. This is shown in Figure 5. The Fe content of the surfaces cleaned using 31 combinations was taken and a second-order regression equation was fitted to it. The R-squared value for the model is around 80 % and hence the model can be considered to have good practical significance. The significance of each term was calculated using ANOVA analysis and the results are shown in Table 2.

The large F-values indicate that the variance of the model is larger than the random error and the model can explain the variation in M_{Fe}. Therefore, the model can be considered a good predictor for the iron content of the surface. The probability of error value of the P-value was used to identify the significant terms. Terms that have a p-value less than 0.05 are considered significant. The second-order regression equation for the M_{Fe} in uncoded units after removing the insignificant terms is

$$M_{Fe} = 74.056 - 0.8292 \times P + 0.01562 \times v + 0.5922 \times f + 0.3137 \times h_d - 0.0029 \times f^2 - 1.3466 \times 10^{-4} \times v \times f, \quad (2)$$

where P is the average laser power, v is the scan speed and f is the pulse repletion rate. It can be observed that all the second-order and interaction terms save one each are insignificant for the prediction of M_{Fe}. This equation can be used to predict the extent of oxidation and thereby the appearance (shiny or dark) of the laser-cleaned surface based on the input parameters.

4.3 Surface hardness

The variation in surface hardness during laser cleaning operations of the 31 experimental runs was studied using

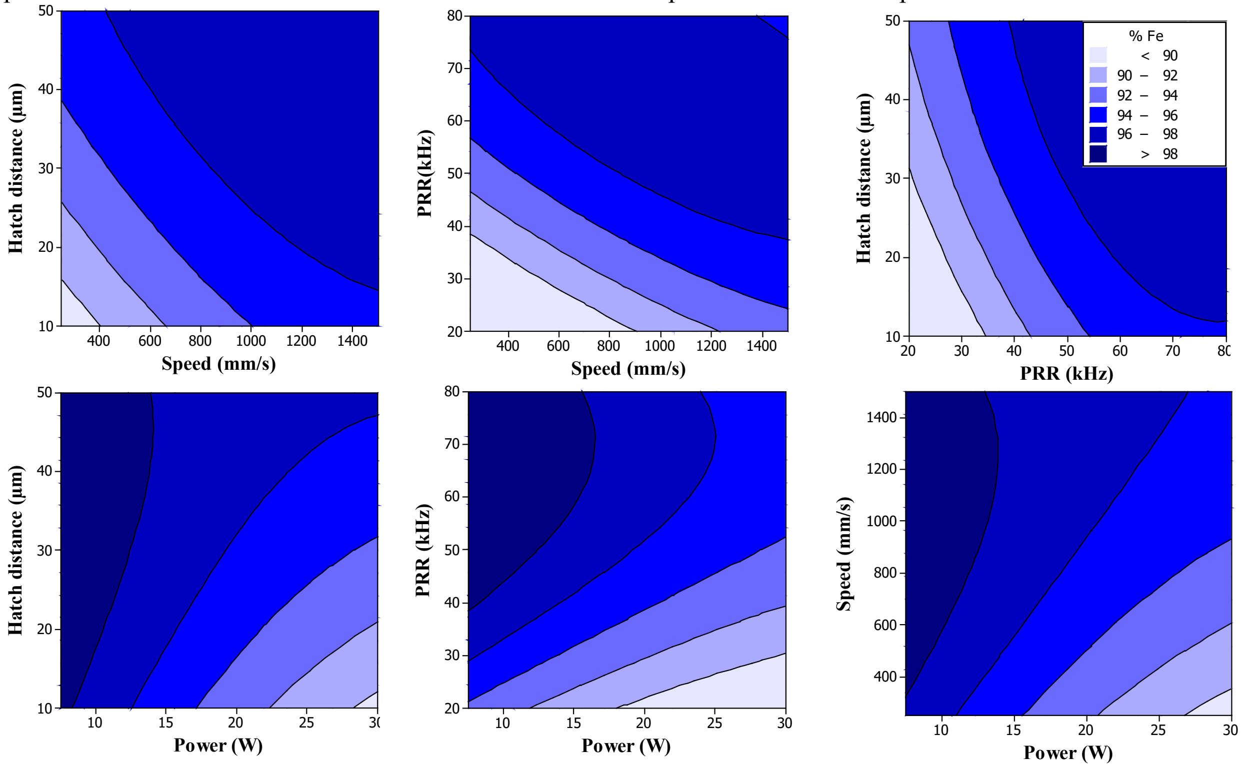

Fig. 5 Contour plot of variation of iron content with different factors (a) h_d and speed, (b) speed and PRR, (c) h_d and PRR, (d) h_d and power, (e) power and PRR and (f) power and speed.

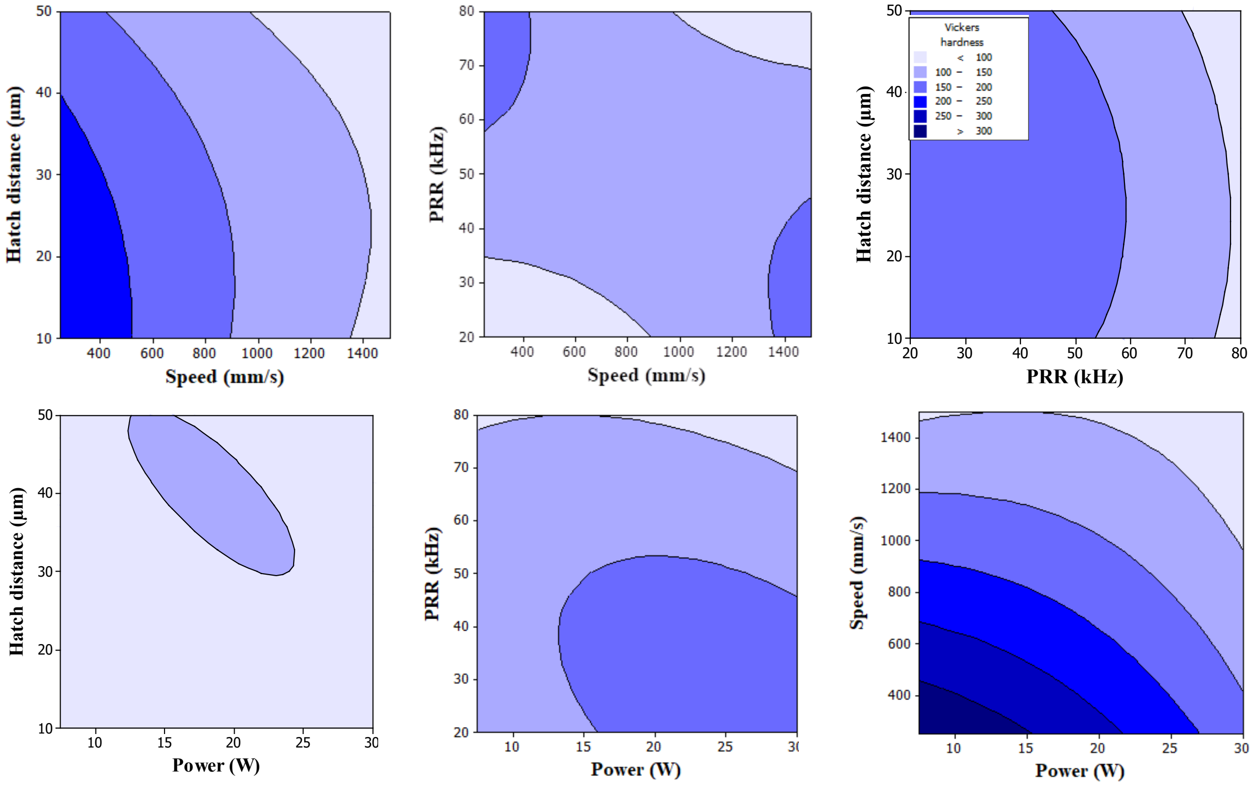

Fig. 6 Contour plot of variation of Vickers hardness with different factors (a) h_d and speed, (b) speed and PRR, (c) h_d and PRR, (d) h_d and power, (e) power and PRR and (f) power and speed.

Table 2 Analysis of variance for $M_{Fe.}$

Source	DF	Adj SS	Adj MS	F	P
Regression	14	646.07	46.148	18.6	0
Linear	4	554.57	138.64	56.1	0
P	1	162.60	162.60	65.8	0
V	1	79.38	79.38	32.1	0
F	1	245.31	245.31	99.3	0
h_d	1	67.28	67.28	27.2	0
Square	4	49.688	12.422	5.03	0.001
P^2	1	1.909	1.909	0.77	0.382
v^2	1	8.648	8.648	3.5	0.065
f^2	1	37.512	37.512	15.2	0
h_d^2	1	3.829	3.829	1.55	0.217
Interaction	6	41.811	6.968	2.82	0.015
$P\times v$	1	4.877	4.877	1.98	0.164
$P\times f$	1	0.152	0.152	0.06	0.805
$P\times h_d$	1	6.308	6.308	2.56	0.114
$v\times f$	1	19.127	19.127	7.75	0.007
$v\times h_d$	1	5.468	5.468	2.21	0.141
$v\times h_d$	1	5.88	5.88	2.38	0.127
Residual Error	140	192.55	2.469		
Lack-of-Fit	10	61.595	6.159	3.2	0.002
Pure Error	130	130.96	1.926		
Total	154	838.62			

Vicker's microhardness test. The surface hardness was observed to increase during most of the experiments. An increase of almost 100 % compared to the initial hardness of ~154 H was observed. However, a few experimental points were observed where the surface hardness decreased by almost 10 % from the initial value. During laser cleaning with nanosecond pulses, a comparatively large melt pool and HAZ are created on the surface. This initiates many physical and chemical mechanisms the effects of which are reflected in the surface hardness. The heating and the high plasma pressure exerted on the surface cause grain refinement similar to laser shock peening. There will also be dislocation movement and accumulation which would result in the formation of sub-micron-sized subgrains. The melting and resolidification would also result in a change in the iron-carbon phase on the surface such as the formation of carbides that would increase the microhardness. When a pulsed laser is scanned over the surface with multiple overlapping pulses, the formation of melt pool and HAZ will be affected by the pulse energy of a single pulse, the number of pulses falling at a given point and the cool-off time between two consecutive pulses. The pulse energy of a single pulse is a function of the average laser power and PRR, the number of pulses falling at a given point and the cool-off time between two consecutive pulses are affected by the scan speed and PRR in the direction of laser scan and by hatch distance in the direction perpendicular to laser scan. The quantitative effect of all the factors on these mechanisms can be observed in Figure 6.

A second-order regression model was fitted to the hardness. The R-squared value for the model is around 84 % and hence the model can be considered to have good practical significance. The significance of each term was calculated using ANOVA analysis and the results are shown in Table 3. The large F-values indicate that the variance of the model is larger than the random error and the model can explain the variation in H. Therefore, the model can be considered as a good predictor for surface hardness. The second-order regression equation for H in uncoded units after removing the insignificant terms (terms with p-value < 0.05) is

$$\mathrm{H} = -62.5365 + 5.9899 \times P - 0.1131 \times v + 7.5989 \times f + 4.2662 \times h_d - 0.130 \times P^2 + 2.7974 \times 10^{-5} \times v^2 - 0.0287 \times f^2 - 0.0414 \times {h_d}^2 + 0.00539 \times P \times v - 0.0594 \times P \times f - 0.1131 \times P \times h_d - 0.00289 \times v \times f + 0.00105 \times v \times h_d \quad (3)$$

Table 3 Analysis of variance for H.

Source	DF	Adj SS	Adj MS	F	P
Regression	14	13237	9455.7	48.79	0
Linear	4	92806	23201	119.7	0
P	1	1074	1074	5.54	0.02
v	1	67925	67925	350.5	0
f	1	22660	22660	116.9	0
h_d	1	1147	1147	5.92	0.016
Square	4	11491	2872.7	14.82	0
P^2	1	1728	2424.8	12.51	0.001
v^2	1	2055	1067	5.51	0.02
f^2	1	5254	5981.8	30.87	0
h_d^2	1	2454	2454.3	12.66	0.001
Interaction	6	28082	4680.4	24.15	0
$P\times v$	1	7201	7201	37.16	0
$P\times f$	1	2010	2010	10.37	0.002
$P\times h_d$	1	3239	3238.5	16.71	0
$v\times f$	1	14715	14715	75.93	0
$v\times h_d$	1	865	864.6	4.46	0.036
$v\times h_d$	1	53	52.8	0.27	0.602
Residual Error	140	27131	193.8		
Lack-of-Fit	10	11094	1109.4	8.99	0
Pure Error	130	16037	123.4		
Total	154	159510			

It can be observed that most of the first-order, second-order and interaction terms are significant for the prediction of the surface hardness. This equation can be used to predict the hardness and thereby the wear resistance of laser cleaned surface based on the input parameters.

4.4 Optimization study on hardness and scan speed

The models were used to optimize the laser cleaning process for the two responses - iron content and surface hardness. The objective is to find the window of parameter values that give a high iron content (~ 99 %) as well as a high hardness (> 300 H). The optimization studies showed that there was a very small window of parameters where the M_{Fe} was almost 99 %. On the other hand, the windows of parameters where the surface hardness is > 300 H are even smaller. The models were used to find the range of parameters where both M_{Fe} and H are in the desired range. The results of the optimization study on M_{Fe} and H with power and scan speed are shown in Fig 7. The holding value of PRR is 80 kHz and hd of 50 µm for this study. It can be observed that for a small range of parameters between 12.5 W and 425 mm/s, the laser-cleaned surface has M_{Fe} > 99 % and hardness > 300 H. This is a very narrow range compared to the full range that was considered in the study. This emphasizes the need for a prediction model based on a treatment combination of different factors for the process optimization of laser cleaning.

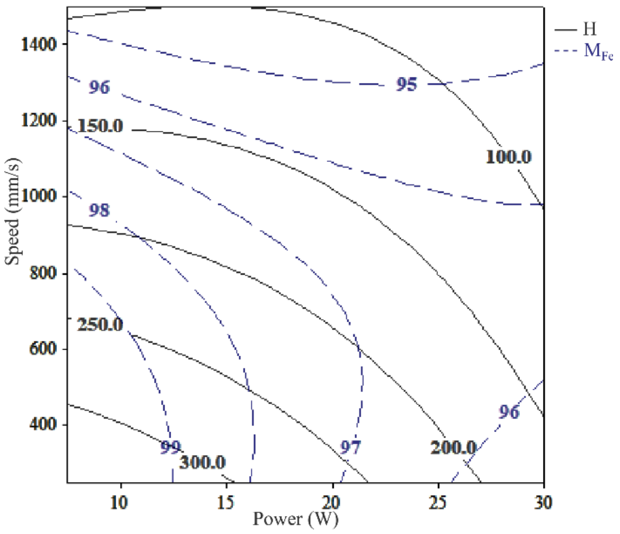

Fig. 7 Variation of M_{Fe} and H with laser and scan speed.

5. Conclusion

The study showed the significance of the interaction effects of laser parameters on the chemical (iron content) and mechanical (surface hardness) properties of the laser-cleaned steel surface. The correlation between the appearance of laser cleaned surface and the iron content of the surface was investigated. The iron content can be controlled by a careful selection of parameters and the probability of getting a shiny or dark surface can be controlled. The study on the treatment combination of four factors, laser power, scan speed, PRR and hatch distance on the appearance and surface hardness of laser cleaned surface showed that the interaction effect is significant for predicting the surface hardness and is insignificant in the case of the oxide content. There exists a small range of parameters at power < 12.5 W, speed < 425 mm/s at a PRR of 80 kHz and hatch distance of 50 µm where the laser cleaning would result in a shiny surface with a hardness value > 300 H.

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