# LASER SURFACE MELTING OF 304 STAINLESS STEEL FOR PITTING CORROSION RESISTANCE IMPROVEMENT

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## 1. ABSTRACT

Laser surface melting has been conducted on a 304 stainless steel (SS) with the aim of enhancing pitting corrosion resistance of the material. This process involves rapid melting of the material's surface followed by rapid solidification to refine the microstructure. This includes the dissolution of inclusions such as MnS, FeS, $Cr_xC_y$, and other minor constituents

The microstructures as a result of laser treatment were observed by means of optical microscope and also confirmed by the XRD. The glow discharge optical emission spectroscopy (GDOES) was utilized for chemical analysis. Changes in hardness were observed by using a Vickers microhardness tester.

Pitting corrosion tests on laser treated and untreated samples were conducted according to ASTM G48-92 to evaluate mass loss and pitting morphology.

Laser surface melting improved the pitting corrosion resistance of this material in a chloride containing environment.

## 2. INTRODUCTION

It is noteworthy that the 300 series austenitic stainless steels are prone to pitting corrosion when exposed to halide ions, particularly chloride ions. This is in fact reducing their applicability in variety of engineering industries. The corrosion properties of steels depend primarily on the microstructure, surface finish and chemical composition of the component.
It is well known that 304 stainless steel was designed to be a low cost material containing 16-18 % of chromium content to resist corrosion. However, it reveals excellent corrosion resistance in ambient conditions, but suffers severe pitting attack in chloride-containing environments [1].

In the last two decades, laser treatment of metals has emerged as a novel surface modification technique [2, 3]. It has been proved that laser surface melting (LSM) or alloying (LSA) is a valuable method to improve wear and corrosion resistance of many metals and alloys. In LSA, the desired alloying elements can be introduced into the molten pool in various forms, and in both solid and gaseous forms. Previous studies have shown that LSM and LSA could be employed to improve the corrosion resistance properties of 304 stainless steels.
LSM involves rapid melting and solidification to produce fine-grained microstructure [4]. This includes the removal or dissolution of inclusions such as MnS, FeS, $Cr_xC_y$, and other minor constituents. The dissolution of $Cr_xC_y$ makes the excess Cr available for the formation of a passive chromium oxide layer. The susceptibility of sensitized 304 and 316 stainless steels to intergranular corrosion is diminished by laser surface

remelting through the dissolution precipitates and inclusions as well as the homogenization of chromium distribution [5]. In the case of 304 SS, pitting corrosion resistance is primarily increased by the formation of δ-ferrite because of its high solubility for sulphur than austenite. This is the reason why microstructural evolution should be studied with due diligence.

The present study is aimed at utilizing laser surface melting to improve corrosion resistance of 304 stainless steel surface. LSM is preferred because it affects the surface only and leaves the bulk material unaffected by heat.

## 3. EXPERIMENTALS

Stainless steel 304L, of 6 mm thickness, was used for this study. The chemical composition of 304 SS is given in Table 1. All the experimental samples for LSM were used as-received without any surface processing. LSM was carried out using a 4.4 kW Nd: YAG laser with a top hat profile beam source. LSM processing parameters were optimized to favour all factors that manipulate pitting corrosion resistance. Figure 1 shows the relationships between various processing parameters. Argon gas was applied into the melt pool to minimize oxidation. Samples of interest were subjected for further studies.
After laser treatment, the samples were sectioned, polished and electrochemically etched with oxalic acid. Analysis of microstructure and chemical composition was carried out by OM and GDOES. The availability of various phases was determined by XRD; Cu Kα radiation was used. Vickers microhardness tester was used for hardness measurements.

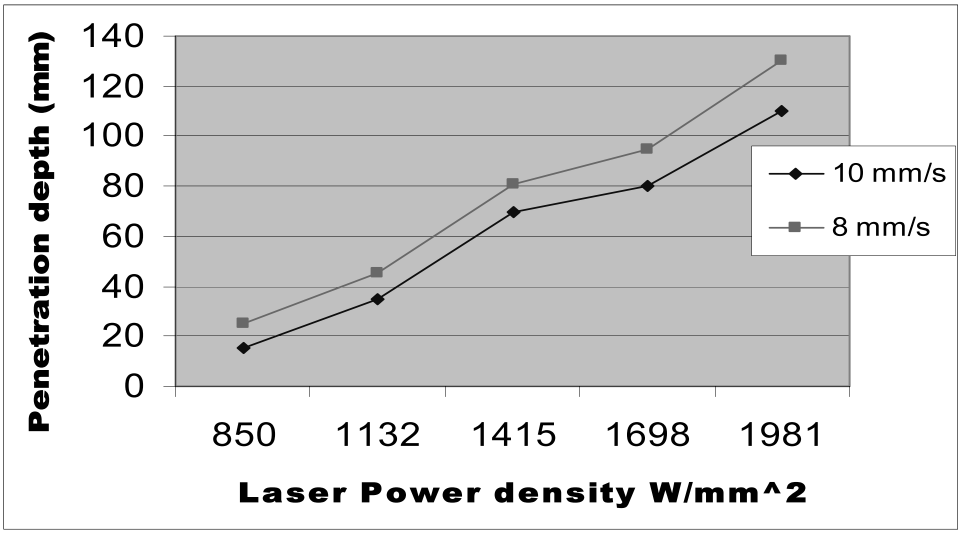



Fig.1. Relationship between laser power density and penetration depth.

Pitting corrosion tests were performed by immersing both laser treated and untreated samples in a ferric chloride solution held at ± 55 $^{o}$ C for 72 hours. This test was performed in compliance with ASTM G48-92 standard. Mass loss test was carried out

to evaluate the pitting tendency of the samples with respect to the conditions of exposure.
Table1:

| Cr | Ni | Mn | Si | C | P | S | Fe |
|---|---|---|---|---|---|---|---|
| 18.4 | 8.5 | - | 0.33 | 0.028 | 0.014 | 0.01 | Bal |

## 4. RESULTS AND DISCUSSION

### *4.1 Microstructural and phase analysis*

The starting material which is 304 SS, exhibit a fully austenitic microstructure with inclusions and precipitates. Fig 2 shows a microstructure of untreated 304 SS sample. Some inclusions are in a form of stringers aligned in the rolling direction of steel

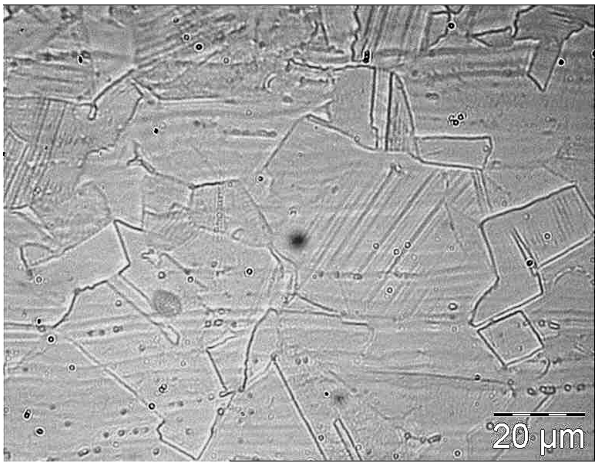



Fig. 2. Microstructure of the starting material showing austenite grains and twin bands.

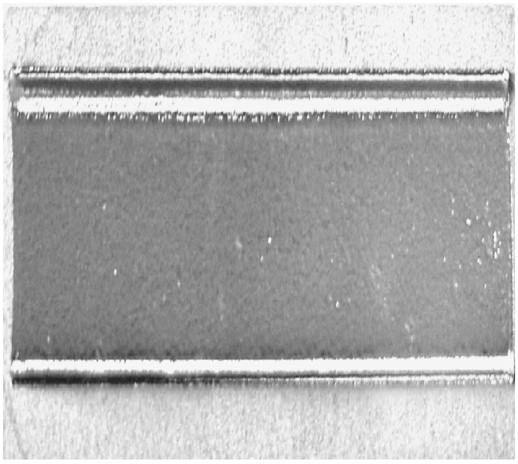


Fig. 3. Laser processed surface under argon atmosphere.

After LSM, the surfaces were silver in colour signifying that the surfaces were smooth and reasonably protected by argon gas. Figure 3 shows this phenomenon.
The cross-sectional microstructures of the laser treated samples in shown in figure 4(a-b).

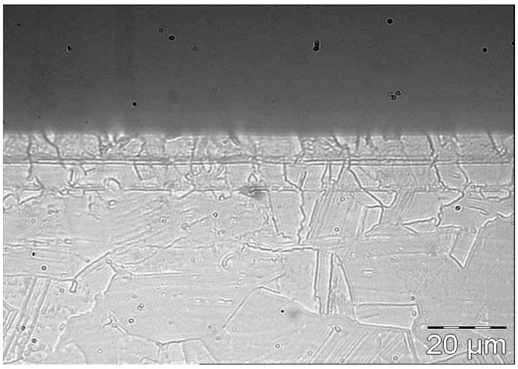



Fig. 4a. Cross-sectional view of sample treated at 2.5 KW travelling at 10 mm/s.

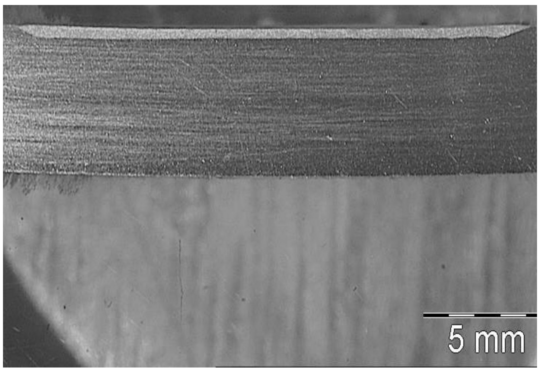



Fig. 4b. Melt pool geometry at the same parameters as 4a.

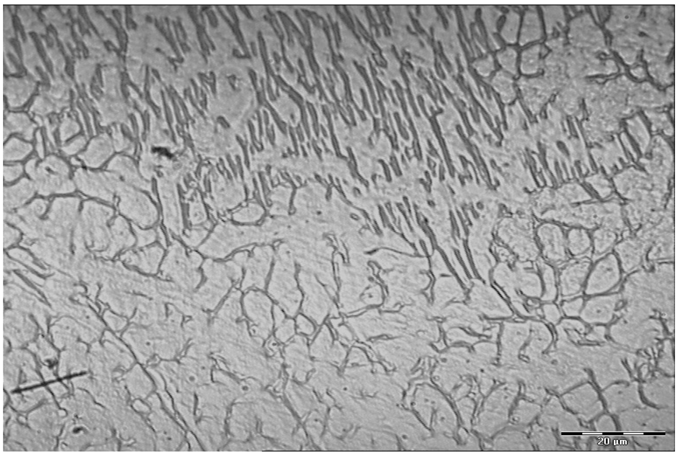


Fig. 5. Microstructure of a laser-melted sample at 1000X.

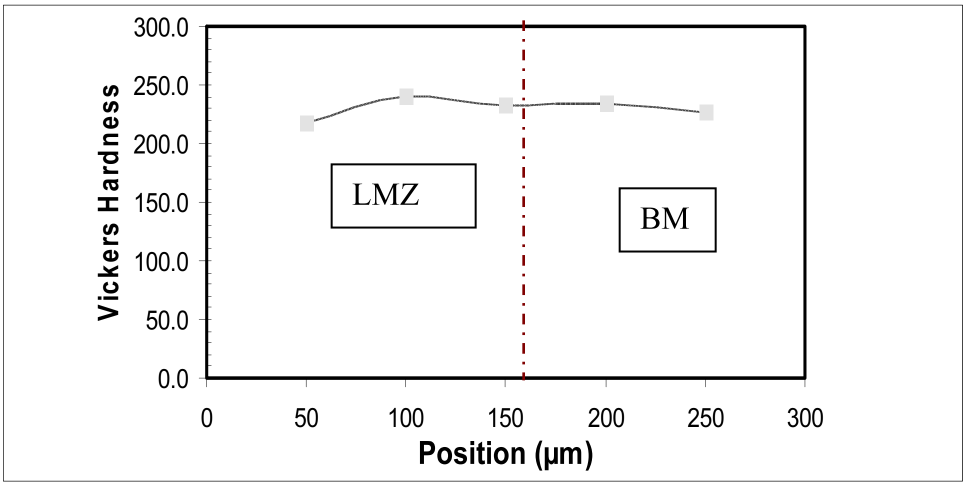
The microstructure of the melted layer given in Fig. 5 shows a network of δ-ferrite in the form of dendritic solidification pattern in the austenite matrix. It is well known that during the solidification of austenitic stainless steels, like AISI 304 the first phase to solidify is delta ferrite δ, as the temperature drops below the peritectic transformation it tends to transform into austenite (γ) [6]. The phase transformation δ ⟶ γ depends on time. As transformation continues at a faster rate, there is less time left for δ ⟶ γ to occur completely, therefore a certain amount of δ phase is retained at room temperature.

During solidification of laser melted 304 SS, the following solidification sequence is followed:

$$L \longrightarrow L + \delta \longrightarrow \delta \longrightarrow \delta + \gamma$$

L- Liquid phase
γ- Austenite phase
δ- Delta iron (ferrite)

Hardness test were performed and there is no change in the hardness value as compared to the base metal. Even though, the structure refinement at the surface could lead to an increase on the yield strength, the hardness measured is not expected to change much particularly in a high strain hardening rate material like this 304 SS. Fig.6 shows a microhardness profile showing the difference in the untreated and laser treated regions.




.Fig. 6. Microhardness across the transverse section of the sample submitted to laser surface melting.

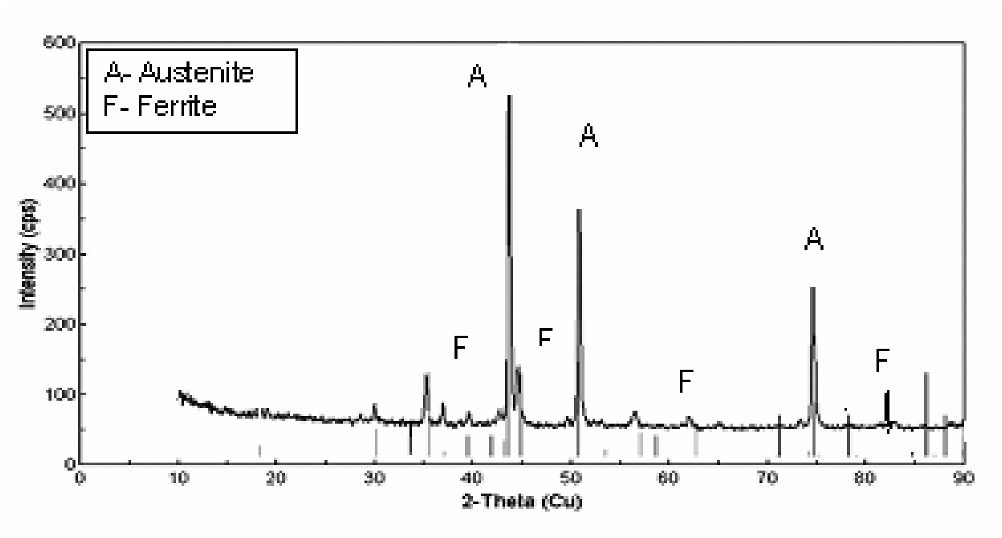
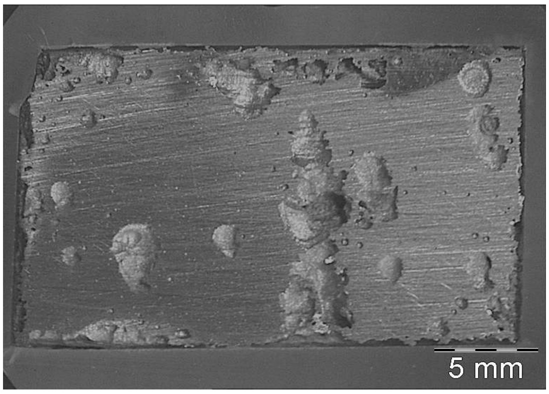



Fig.7. X-ray diffraction spectrum of a laser treated 304 SS.

The XRD spectrum in Fig 7 confirms the existence of delta ferrite phase in the austenite matrix. The spectrum of untreated 304 SS shows the austenite peaks only, but because this sample has been subjected to laser surface melting, delta ferrite peaks are introduced.

## *4.2 Corrosion tests and surface chemical analysis*

Corrosion tests were carried out to investigate the pitting behaviour of the laser-melted and as-received 304 SS samples. Rectangular-shaped samples were machined to the same surface are and mass for a comparative study. These samples were cleaned ultrasonically and immersed in a ferric chloride solution held at ± 55 $^{o}$ C for 72 hours. Fig.8. shows the pitting morphology of both laser treated and untreated samples after 24 hours of exposure in testing media.



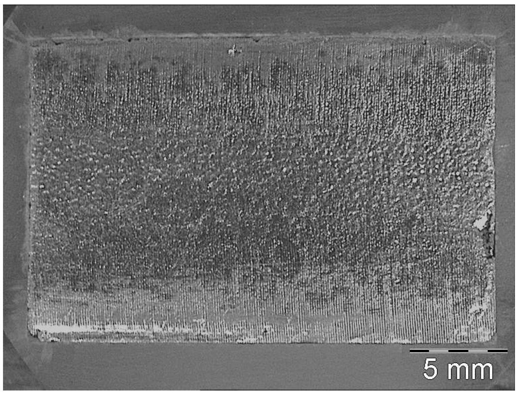




Fig.8. a) Untreated 304 SS surface. Fig.8. b) Laser treated 304 SS surface.

After 48 hours, it was apparent that laser-melted sample resisted pitting. On the other hand, the untreated sample showed randomly dispersed pits which are deep in geometry. Fig.9 illustrates mass loss for both samples exposed for 72 hours.

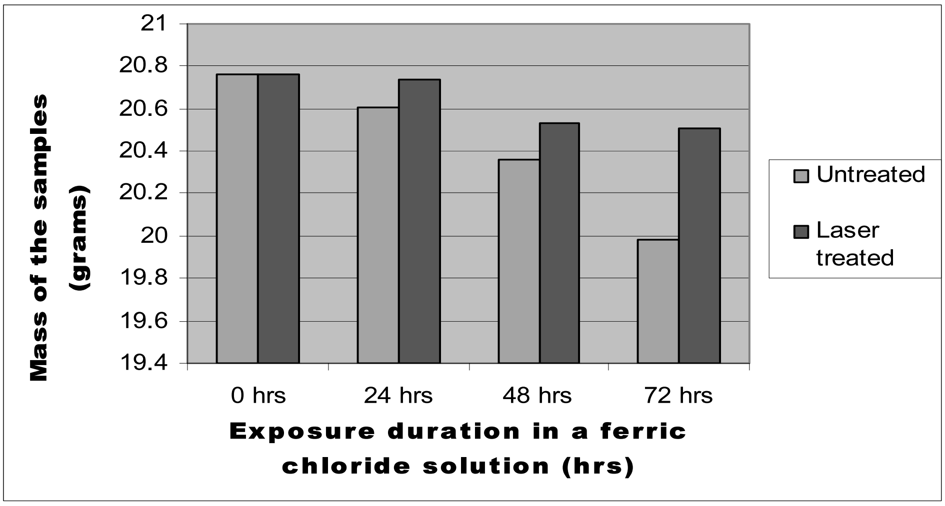
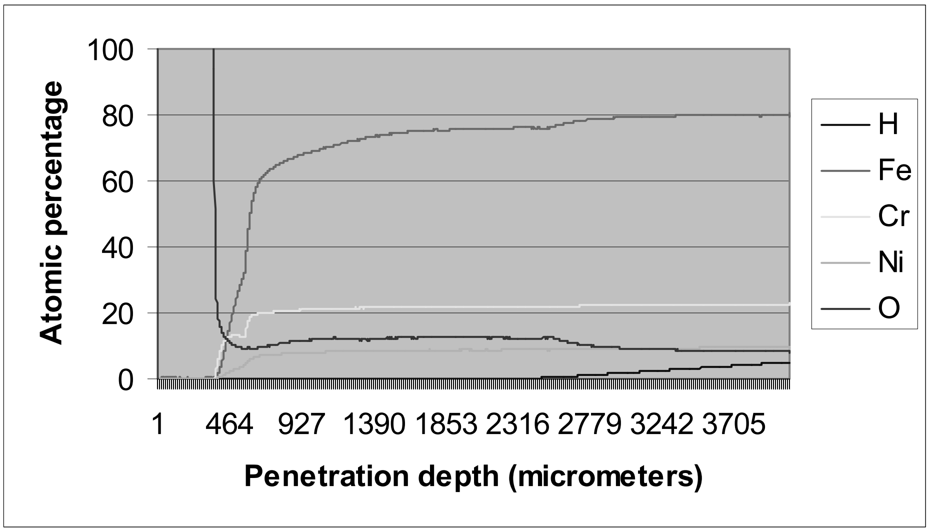



Fig.9. Shows the tendency of losing mass between the untreated and laser treated samples.

Both samples started the test with the same mass, which gives this comparative study more sense. It is clear from the illustration that after 48 hours, a laser treated sample has lost only few milligrams. In this stage the passive layer on the surface was still strong as compared to the untreated sample. This is because during LSM, chromium tends to react with oxygen to form a passive chromium oxide layer. The removal and dissolution of inclusions and precipitates contributes a lot. After 72 hours, a laser treated sample started to corrode at an accelerated rate. This sample showed smaller and shallower pits in clusters.
The foremost factor is the microstructural transformation which has led to the formation of a desirable quantity of delta ferrite.

Corrosion is also related to chemical composition. The chemical composition in delta ferrite region and as well as in the pits area plays a mayor role accelerating this behaviour. Therefore a detailed chemical analysis should be conducted to show the effect of certain elements on corrosion properties of this material. Fig. 10 shows a graphical illustration of the glow discharge optical emission spectroscopy (GDOES). This analysis provides chemical information from the surface penetrating to more than 100 micrometers.




GDEOS utilizes low-pressure, non-thermal process in which materials uniformly sputtered from the sample surface by a stream of argon ions from plasma. The cathodic sputtering removes the material layer by layer, without any changes in sample chemistry caused by melting. Therefore the light emitted from this excitation is analysed using an optical emission spectrometer.
The percentage of chromium and nickel show a uniform distribution from the surface penetrating the sample.
An oxide layer represented by a percentage of oxygen at the near surface layer.

## 5. CONCLUSIONS

(1) Laser surface melting (LSM) has improved the corrosion resistance of 304 SS.
(2) Surface melting of 304 SS with a 4.4 Kw laser produced a duplex microstructure with retained delta ferrite at the dendritic boundaries.
(3) The formation of delta ferrite in the austenite matrix has led to this improvement of pitting corrosion.

## 6. ACKNOWLEDGEMENTS

The author is grateful to the CSIR National Laser Centre for supporting this work.

## 7. REFERENCES

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