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## Effect of Laser Surface Melting on Chromium Carbide of 304 Stainless Steels

**Abstract-** In the present study, the effects of laser surface melting (LSM) on chromium carbide of heat treated (AISI 304) austenitic stainless steels (ASS) was studied with the aim to suppress sensitization of 304SS. Austenitic stainless steels were heated (aging) up to (800) °C at constant holding time for two hours. LSM was conducted by using a (600 W) Yb-YAG laser. The microstructure was characterized by using optical microscopy (OM), scanning electron microscopy (SEM) and X-ray diffraction (XRD). Results shows, refined and homogeneous microstructure which contains austenite ( $\gamma$ ) as basically phase and delta ferrite ( $\delta$ ) as the secondary phase, however, chromium carbide ( $Cr_{23}C_6$ ) phase are fully dissolved. Desensitization of heat treated ASS has been successfully achieved by LSM which reduced Cr depletion at the grain boundaries..

**Keywords-** Stainless steel, Laser, Surface melting, Corrosion, Pitting, Sensitization, Chromium Carbide, Delta ferrite, solidification mode, Surface Engineering.

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**1. Introduction**

Austenitic stainless steel (ASSs) (18 wt.% Cr, 8 wt.% Ni) is Fe–Cr–Ni alloys. It is one of the most commonly used ferrous materials for many industrial application like the petrochemical and chemical industries, marine, desalination and nuclear plants, and novel thermal sensors owing to their perfect weldability, excellent resistance of corrosion and mechanical properties [1-4], but, type 304 stainless steel, in some cases like incorrect thermal treatment, a sensitization trouble occur, then susceptible to localized attack, and thus, failure of industrial materials [5,6].

Sensitization happens by ( $Cr_{23}C_6$ ) precipitation at grain boundaries throughout the slow cooling within the 450-900C° temperature. Sensitization temperature may be reached throughout manufacture operations and additionally slow cooling from higher temperatures [7-10]. ( $Cr_{23}C_6$ ) precipitation causes a chromium-depleted regions neighboring to the grain boundaries, thereby lowering Cr content of the surface oxides over these regions. If the content of chromium in the regions adjacent to the carbides drop below 12 wt%, the oxide layers lose their protection. Then the stainless steels will suffer for localized corrosion. Conventionally, sensitization can be solved by following steps [8, 11-13].

1. Using high-temperature solution treatment and a sufficiently fast cooling to be applied to dissolve the chromium carbides.

2. Adding carbon stabilizing elements, which have a more affinity to carbon than to chromium.

3. Using low –carbon varieties.

However, these methods are not always possible, and impractical for large parts, in addition, the high thermal stresses may be introduced because of rapid quenching, in these conditions, an in-situ way is necessary to selectively desensitize the microstructure [5, 13, 14].

An alternative process to avoid the sensitization is Laser surface melting (LSM). It is an effective way for removing the sensitization. Desensitization is successfully accomplished by LSM, which dissolves the carbides and restores the chromium levels. [7,15-18] By LSM, a sensitized region may be melted in ambient environments. It is, economical, simple and efficient fast solidification process of the surface causes solid solution of the alloys system, formation of homogenized and refined microstructure and redistribute/dissolve the precipitates while the substrate properties can be protected [19-23]. LSM permits selective melting and heating of the surface that modifies the surface properties of the alloy due to fast melting and solidifying [14, 24-26]. By LSM, the molten surface is protected by inert gas, by employing this method, little thermal penetration; can be obtained, resulting in small distortion [27]. Surface properties display a high dependence on the composition and microstructure of the alloy surface and near-surface zone. Through LSM, a

thin surface layer rapidly melts by high power of laser beam, and the remaining material supplies self-quenching at cooling rate ranges from 103 – 106 °C/s depending on the thermo-physical properties of the substrate material and the traversing rate of the laser. The Cooling rates are basically depend on the laser parameters. Formation of austenitic microstructure is very sensitive to the cooling rates. A little change in cooling rate can lead to high change in solidification mode and result differences in the microstructures. A surface modified layer with fine structure and high surface properties can be produced with appropriate laser parameters [9, 14, 28].

## 2- Experimental

In this work, a plate of AISI 304 stainless steel of 3 mm thickness is used. Table 1 shows the chemical composition of as received of AISI 304ASS.

Samples were cut with dimensions of (100×40) mm in order to be heat-treated, laser surface

melted and subsequently examined and test. They are exposed to heat (aging) processes using electric resistance furnace at temperatures (800) °C at constant holding time for two hours and then left to cooled to room temperature and prepared to subsequent processes.

The processes of laser surface LSM melting were performed using a Yb-YAG laser type (YFL-600W CW Fiber Laser) with an output power of 600 W and continuous wave (CW) with (1080) nm wavelength. Argon gas has been used as a shielding and protecting gas. Different experimental parameters of laser surface melting were used in sixteen tracks to obtain optimized melting region. The parameters of optimized melting region are: power (530) W, spot size (1.5) mm and scan speed (20) mm/s. After that the samples were prepared for the subsequent examinations and tests.

**Table 1: Chemical composition of AISI 304 Stainless Steel Used**

Element (wt. %)	C%	Cr%	Ni%	Mn%	Mo%	P%	Si%	Fe%
measured	0.06	20	10	1.27	0.0	/	/	balance

### I. Microstructural Examinations

The microstructures of as received specimens, aged and of laser processes are characterized and identified by using scanning electron microscopy (SEM), optical microscopy (OM), and X-ray diffraction (XRD). The specimens are prepared for (OM) and (SEM), for microstructure examinations in the conventional methods. The micrographs of all are picked using optical microscope, which contains an electronic camera connected to computer

### II. XRD examination

The X-ray diffraction (XRD) examination was done in order to find out the phases identifies each specimen to determine the effects of different processes on modification microstructure and find phase transformation. Examining was done on of the three types of specimen: as received, after aging process and after laser surface melting. Phases were identified by using Standard XRD patterns.

## 3. Results and Discussion

### I. X-ray diffraction analysis

The results for (XRD) tests before and after heat treatment processes are shown in Figure 1. Figure

(1-A), shows the result before heat treating. It is observed that there is only single phase (austenite  $\gamma$ ) existed in matrix before heat treatment. Figure (1-B), shows the presence of a new phase in the microstructure after heat treatment, this indicates that phase transformation occurred in the microstructure, due to the thermal effect. Chromium carbides ( $Cr_{23}C_6$ ) were found (in addition of  $\gamma$  phase), and this is because of the great ability of the chromium atoms to diffuse and interact with the carbon atoms. This is due to the thermal effects that occurred in thermal grades in which the aging process have taken place. It leads to the formation of chromium carbide phase and it's precipitation on the grain boundaries. Chromium movement from regions neighbor the grain boundaries leads to the depletion of chromium in these regions. The phenomenon of carbides coming out of the solid solution occurs when austenitic stainless steel has been exposed for a period of time within the specific range of thermal grades and slowly cooled. This will make the grain boundary depleted of chromium. Figure 2 shows the results of XRD after laser surface melting LSM, It is observed that a clear change in general graphic of the XRD compared to that before laser treatment. Moreover, it is similar to

XRD graph of as received 304SS, which shows only austenite peaks as shown in Figure 3. In XRD after LSM, the most important remarkable (in addition of the presence of peaks of austenite phase  $\gamma$ ) are two cases: first, the complete disappearance of the carbides phases, and second appearance of a new phase known delta Ferrite ( $\delta$ ). These changes are due to the effect of laser surface melting process, as a result of the mechanism of melting and rapid solidification.

For the first case, the phase of chromium carbides was completely disappear. Because of the temperature during LSM exceeds the melting point of 304 SS, chromium carbide was dissolved, and chromium atoms moved from grain boundaries to grain matrix by the mechanism of diffusion process within LSM, and because of the rapid solidification due to the LSM process, there was not enough time available for chromium carbide to form and precipitate again, thus a microstructure free of chromium carbide was obtained [8]. For second case, in which delta ferrite ( $\delta$ ) appeared, the condition and mechanism of ( $\delta$ ) phase formation is referred to the mechanism and type of solidification mode during LSM, solidification mode can be expected by employing chromium/nickel equivalents ( $Cr_{eq}/Ni_{eq}$ ) ratio, this ratio can be calculated by using equations 1 and 2 [7,29-32].

$$Ni_{eq} = Ni + 30C + 30N + 0.5Mn \quad (1)$$

$$Cr_{eq} = Cr + Mo + 1.5Si + 0.5Nb \quad (2)$$

According to the above equations and the composition of 304ss that used in this work, the  $Cr_{eq}/Ni_{eq}$  ratio is about 1.56, and then solidification mode falls within (FA) mode of solidification types.

In this mode, precipitation of primary dendritic delta ferrite ( $\delta$ ) should solidify first, and then with the continued temperature drop, the transformation tends to austenitic ( $\gamma$ ). The peritectic transformation of  $\delta$  phase to  $\gamma$  phase depends on diffusion during solid or liquid phases. This means that the transformation depends on time. Under non-equilibrium solidification conditions, transformation of  $\delta$  to  $\gamma$  phase is incomplete because the diffusion is suppressed by the very high cooling rate, and then, no enough time for the complete transformation of  $\delta$  to  $\gamma$  phase. Therefore, it could be expected that the amount of delta ferrite was retained at room temperature. The (AF) solidification mode occurred as following sequence: [33].

$L \rightarrow L + \delta \rightarrow L + \delta + \gamma \rightarrow \gamma$  (major) +  $\delta$  (minor)  
Where L: Liquid phase.

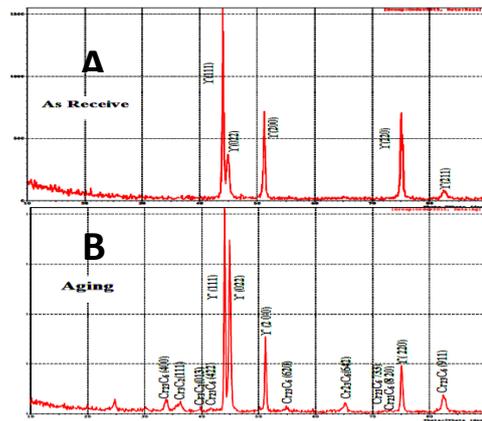


Figure 1: XRD A- before and B- after heat treated

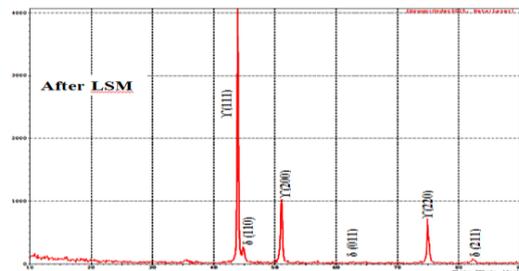


Figure 2: XRD after LSM

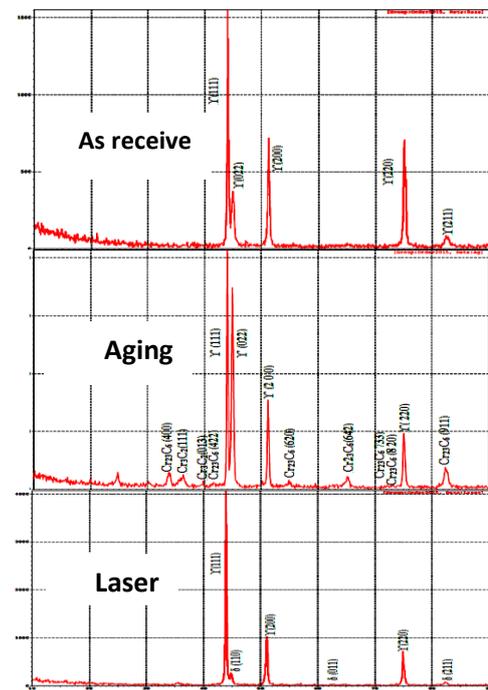


Figure 3: XRD, as receive, aging and after LSM

II. Microstructural Examination

Figures 4 and 5 show SEM and the (OM) microstructure respectively after heat treatment process. These figures show changes in microstructure representing grains boundaries shown appearance of new phases as discontinuous dark lines. Chromium carbide is the new phase as determined in XRD examination and the reasons of their formation was discussed in the previous section. After LSM, a homogeneous microstructure was observed, and free from cracks or defects, which can be seen with the naked eye. The typical transverse cross-section is shown in Figures 6. It shows two regions: melted and sensitized region. After LSM, microstructures of melted regions were refined and more homogenized. In addition, the chromium carbides completely dissolved due to rapid cooling. Through LSM; a thin surface layer reached temperatures more than the melting point, then all carbides in the melted pool are decomposed.

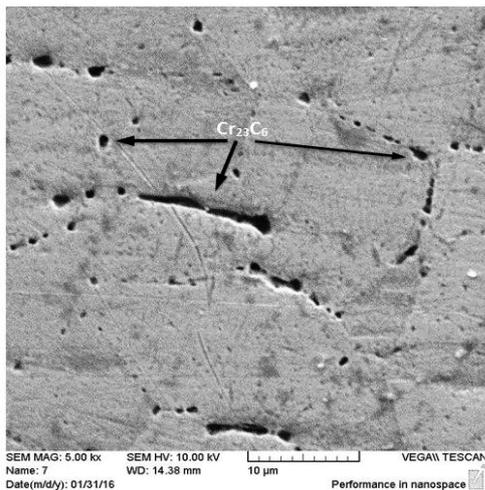


Figure 4: SEM after heat treated

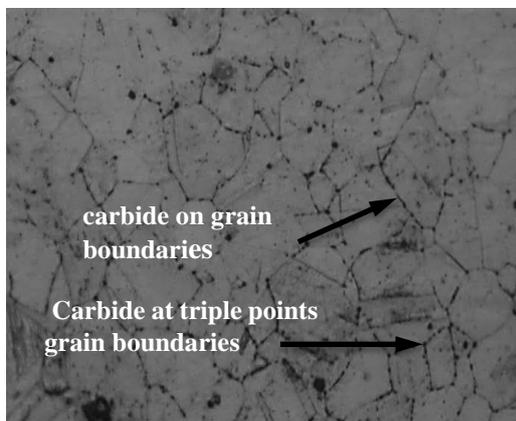


Figure 5: sample after heat treated (aging) at 800°C for two hours

After LSM, in detail notice, that the melted regions reveals fine dendritic microstructure, as shown in Figure 7. This region consists of columnar grains growth, which can be seen in the melted region. Fine dendrites were observed within these grains. Figure also shows the morphologic transition from the boundary between the bulk, and melted region toward the top surface of fusion zone. Because of the change in the thermal gradient and cooling rate, Various morphologies can be seen along cross section, figure (7-A) shows Random dendrites near the surface, a Cellular/dendritic in the center of melting zone can be seen as shown in Figure (7-B), while (7-C) shows columnar dendritic between the center of melted zone and substrate.

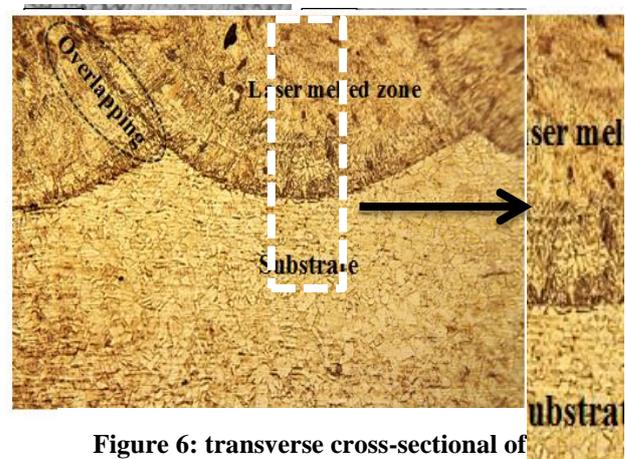


Figure 6: transverse cross-sectional of microstructure after LSM



Figure 7: shows various forms of microstructure

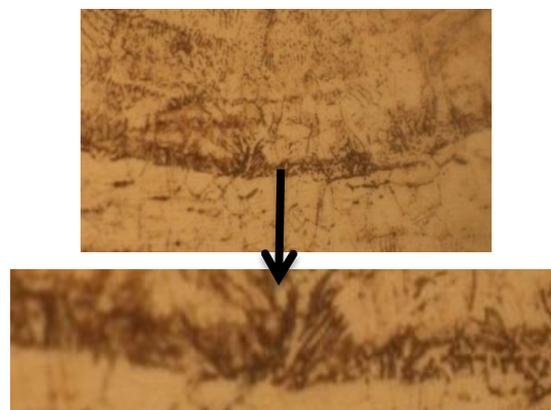
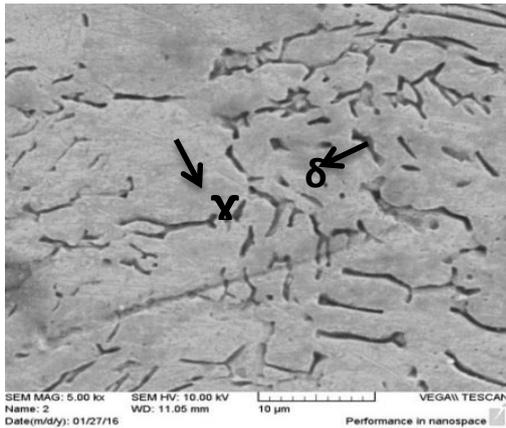


Figure 8: interface zone between melted and substrate



**Figure 9 SEM micrographs shown  $\delta$  and  $\gamma$  phases**

#### 4. Conclusions

The conclusions of this present work can be summarized as follows:

1. Chromium carbides are completely disappeared after laser surface melting, and chromium element redistributed in austenite structure.
2. Refined and homogenized microstructure was achieved after laser surface melting in the melted zone.
3. Variety of microstructure morphologies were obtained along cross section of melting layer from interface zone at substrate toward surface melting zone.
4. After laser surface melting a certain amount of  $\delta$ -ferrite formed in the austenitic microstructure and reside at room temperature.

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