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Prediction the Initiation of Pitting Corrosion Depending on Carbides in the Microstructure of 304 Stainless Steel

Abstract- *Stainless steel has excellent corrosion resistance due to formation oxides protective films in many environments. When steel exposed to temperature in the range of (500-900) ºC, the carbon in the structure will be effective to react with chromium in the structure , which is no less than 18.6% in the present used steel, to form chromium carbides in different types ($M_{23}C_6$, M_7C_3, $M_{2.9}C$) in which M represent chromium. Therefore pitting corrosion will be initiated due to two reasi, the first was depleted zone and the second is galvanic effects between carbides and matrix. The present work was aimed to find relationships to predict the initiation of pitting corrosion depending on carbides in the microstructure of 304 stainless steel, which formed in heated specimens at (500 - 900) ºC. The potentiodynamic cyclic polarization (PCP) measurement was performed to investigate and analyze pitting corrosion resistance properties.*

Keywords- *stainless steel, sensitization temperature, depleted zone, Cr- carbides, galvanic effect, pitting corrosion.*

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1. Introduction

Austenitic stainless steel is the most common among stainless steel and characterized by an excellent corrosion resistance [1, 2]. The austenitic structure is stabilizing at room temperature. If austenitic stainless steel heated or welded or used in higher temperature leads to formation of sensitization phenomenal. Sensitization is grain boundary depletion of chromium and precipitation of chromium carbides near or at grain boundaries. Sensitization refers to the breakdown in corrosion resistance due to depletion of chromium by the formation, growth and precipitation of chromium carbides particle in the grain [3, 4]. When steel encounter temperature in range of about (500-900) ºC most notability in the (Haz) of weld in addition to the loss in corrosion resistance due to chromium depletion [5]. The Cr carbides is a Cr-enriched ($M_{23}C_6$, M_7C_3, $M_{29}C$) in which M represent chromium and some small amount of Fe. Within the sensitization temperature rang carbon atoms rapidly diffuse to grain boundaries, where they combine with Cr to form Cr-carbides. Because of Cr carbides precipitation at the grain boundary the area adjacent to the grain boundary are depleted of Cr and easily to cored [6]. The effect of the formation and the enrichment of the metallic carbide on the pitting corrosion resistance properties of austenitic stainless steel were debated. However, pitting corrosion behavior depending on austenitic stainless steel microstructure that particularly developed through the effect of heat treatment with different temperature through preheating of sensitization. The main aspect of the study is to investigate correlation against pitting corrosion resistance and micro structural features that affected by duration temperature of sensitization heat treatment.

2. Experimental Work

I. Materials

Stainless steel plates (AISI 304) was bought from the market for the purpose of the experiments. The bulk stainless steel is 2 mm thick which were cut into several samples to dimensions of 1.5*1.5 mm. The chemical composition of the 304 stainless steel has been measured by oxford instruments. Table (1) shows the results of analytical stainless steel type 304compared with ASTM standard.

II. Heat treatment

Heat treatment was done at rang of temperatures in order to make it sensitive to produce chromium carbides in the structure. The samples were placed inside the furnace for heated to several different temperatures began from (500, 600, 700, 800 and 900) ºC respectively. Thermal furnace Type (CARBOLITE FURNACE) was used. The installation was for an hour of time then were cooled slow cooling inside the furnace to room temperature.

III. Grinding

Grinding process was done by using disk rotary instrument with water using paper SIC silicon carbide paper varying degrees of smoothness began 220, 320, 500, 800,1000, and 1200 respectively.

IV. Polishing

The polishing was done by using polishing cloth utilize, Damon and refine oil with cloth paper. Light pressure was implemented till the surfaces were freed from scratches. The samples have been clean, dried then examined under the microscope.

V. Etching

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The etching is a process that examine the crystalline border using chemical solution, consisting of 50 ml HNo_3 and 50 ml Hcl has obtained for the purpose of showing the microscopic structure of austenitic stainless steel 304. The specimen were immersed in the solution for a period of (40-45) seconds and then was washed with water, alcohol and then dried by dryer. The microstructure evolution was examined by means of a metallographic microscope utilizing microscope (Kruss).

VI . Cyclic Polarization test

Cyclic Polarization test was performed using Tafel extrapolation method to investigate pitting corrosion properties of sensitized specimens. Sulfuric acid solution was prepared. This acid diluted to 1N aqueous solution of H_2SO_4.

Table 1: Analytical results of 304 stainless steel and Standard ASTM

Elements %	Results	Standard ASTM
C %	0.041	0.08 Max
Si %	0.459	1 Max
Cu %	0.111	0.12
Mn %	1.07	2 Max
P %	0.040	0.045 Max
S %	Less 0.0005	0.03 Max
Cr %	18.6	18 – 20
Mo %	0.066	0.38 Max
Ni %	8.67	8 - 10.5
Ti %	0.006	------
N %	Less 0.010	0.05 Max
Fe %	Remainder	66.34 – 75

3. Results and Discussion

I.Effect of Heat treatment on microstructure of 304 stainless steels

Figure (1) shows the microstructure of 304 stainless steel as received and sensitive specimens. From this figures it can be seen that the microstructure of as received had fine and homogenous grains of austenitic stainless steel. There are no carbides in the microstructure or on the grain boundaries. The effect of heating temperatures (500, 600,700 800 and 900) °C on microstructure of stainless steel show that as sensitive temperature increases, the microstructure become inhomogeneous due to chromium carbides precipitation at grain boundary as shown in Fig. (1). It was shown as dark areas in the microstructure.

Figure (2) shows the microstructures analysis of sensitized samples. The percentage of carbides as results from Image analysis program is given shown in table (2). The enrichment of precipitation of carbides increased due to the increasing the temperature of sensitization. The XRD examination confirms that the formation of coherent precipitation of $Cr_{23}C_6$, Cr_7C_3, $Cr_{2.9}C$ on the grain boundaries as shown in Fig (3)

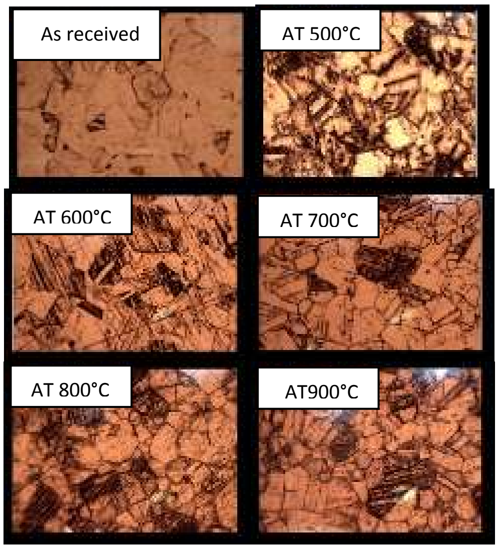


Figure 1: Microstructures after heat treatment at 400X

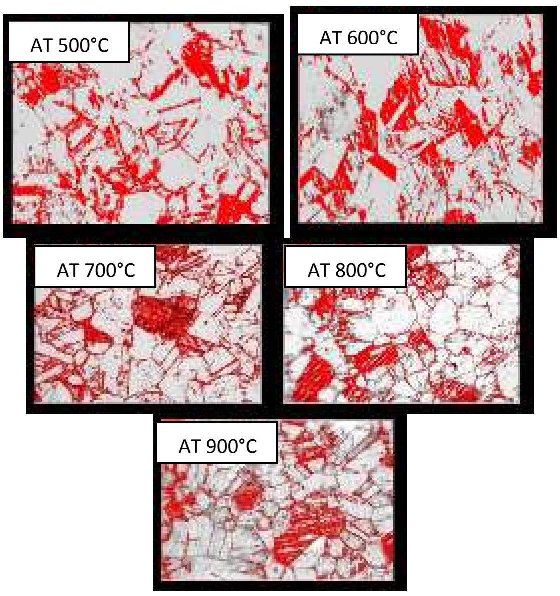


Figure 2: Image analysis of sensitized samples at different condition.

Table 2:The percentages of carbides as a function of sensitization Temperatures

Condition of the sample	Percentage of carbides %	Type of carbides
As-received	No carbides	No carbide
Heat treated at 500 ºC	12.23	Cr_7C_3 , $Cr_{23}C_6$
Heat treated at 600 ºC	13.17	Cr_7C_3 , $Cr_{23}C_6$
Heat treated at 700 ºC	16.16	$Cr_{2.9}C$, Cr_7C_3 , $Cr_{23}C_6$
Heat treated at 800 ºC	17.22	$Cr_{2.9}C$, Cr_7C_3 , $Cr_{23}C_6$
Heat treated at 900 ºC	17.91	$Cr_{2.9}C$, Cr_7C_3 , $Cr_{23}C_6$

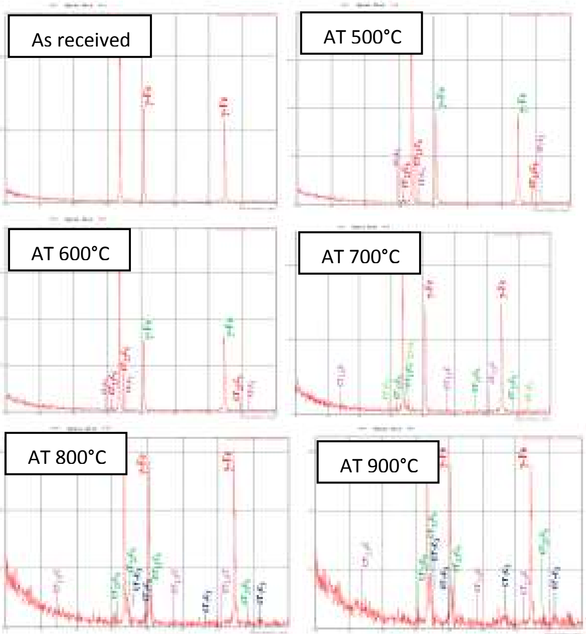


Figure 3: XRD pattern at different condition

II. Corrosion behavior analysis

The correlation between microstructural and pitting corrosion resistance proved that unsensitized structure had low susceptibility to pitting corrosion. Unsensitized specimens showed that the austenitic structures were perform well in resisting pitting corrosion attack. Fully austenite structure performs good corrosion resistance for 304 stainless steel [7]. The heating of specimens to sensitization temperature range (500 – 900) C led to precipitation different types of chromium carbides like $Cr_{23}C_6$, Cr_7C_3, $Cr_{2.9}C$ on the grain boundaries. As increase in sensitization temperatures the nucleation of pitting corrosion increase as shown in fig (5). Figure (4) show corrosion behavior of austenitic stainless steel sensitized at different condition in 1N H_2SO_4. Table (3) represents the pitting current density and pitting potential that we got from the polarization curve.

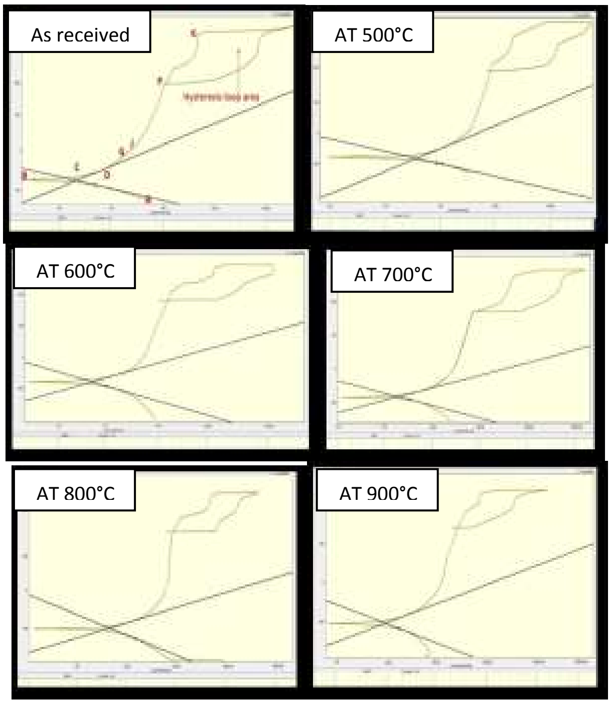
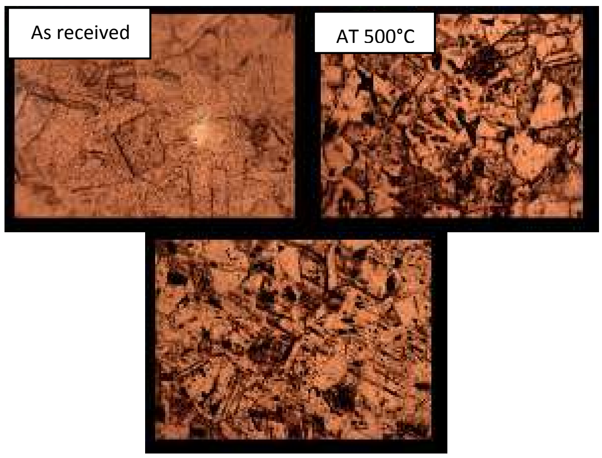


Figure 4: corrosion behavior of austenitic stainless steel sensitized at different condition in 1N H_2SO_4

Table 3: the pitting current density and pitting potential

CONDITION PARAMETER	I_{pit} mA/cm^2	E_{pit} mV
As-reseived	$9*10^{-1}$	1010
At500ºc	$6*10^{0}$	978
At 600ºc	$1.3*10^{1}$	946
At 700ºc	$6.7*10^{1}$	886
At 800ºc	$9.6*10^{1}$	811
At 900ºc	$2.6*10^{2}$	726



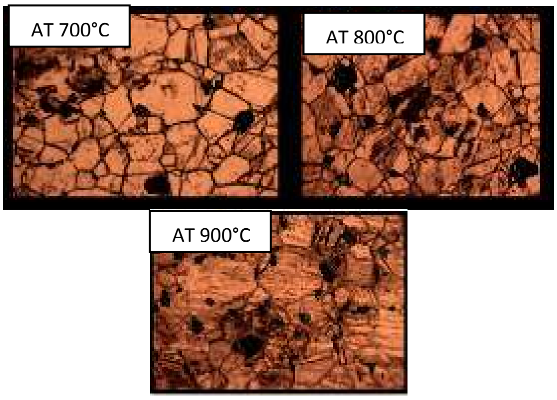


Figure 5: Microstructures after corrosion at 400X

The heating temp. affacted on the numbers of pits and their sizes as shown in table (4).

Table 4: illustrates number of pits and mean pitting diameters.

Specimen Condition	Number of pits	Mean pitting diameters, µm
As received	98	0.31
At 500 °C	344	2.247
At 600 °C	387	3.738
At 700 °C	481	4.879
At 800 °C	511	6.288
At 900 °C	579	7.901

This relationship between amount of carbides and number of pits shown in Fig (6), which follows the following equation;

y = 0.15786*x^3 + -3.8319*x^2 + 44.202*x + 97.935

Norm of residuals = 0.416

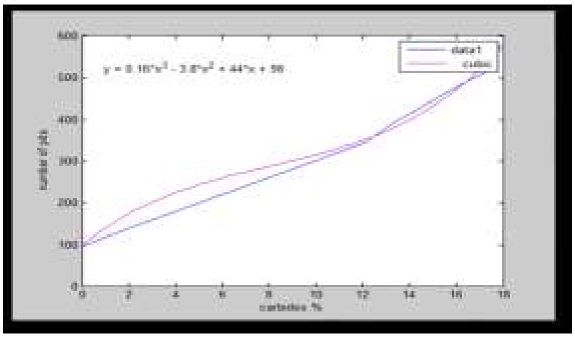


Figure 6: Number of pits as a function of carbide percentage

This relationship depends on the relationships between the heating temperatures and amount of chromium carbides as shown in table (2).

The size of pits depends on the size of carbides as shown in Fig(7), following equation;

y = 0.0021697*x^3 + -0.029479*x^2 +0.22958*x + 0.2978

Norm of residuals = 0.108

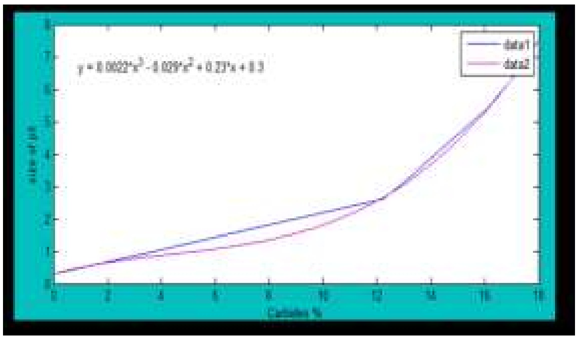


Figure 7: size of pits as a function of carbides

In work [8] conformed that when the specimens of AISI 304 stainless steels specimens exposed to medium containing sulfite anion (H_2SO_4). The pitting mechanisms of austenitic stainless steels are always related to formation of chromium carbides and depletion of Cr at the adjacent grain boundary. However, when the amount of carbides nano particles increased this means that amount of chromium depletion zones increased. Therefore, when heat sensitization temperatures increased from 500 °C to 900 °C the depleted zones of Cr were increase and large numbers of nanoparticles size of carbides would be precipitated. Localized corrosion would be appeared in depletion zones of chromium due to lose of this high corrosion resistance element from one side, and from other side this element would be reacted with carbon in the microstructure to form chromium carbides, which precipitated on the grain boundaries .The precipitates of chromium carbides would be caused galvanic effect due to different potential between these carbides and the matrix. These two phenomena will encourage to formation pitting corrosion, therefore carbon contentplay the main resin of initiation of pitting corrosion. Correlating the microstructural behavior to pitting corrosion resistance behavior, increasing temperature of sensitization caused detrimental on the microstructure which directly reduce the pitting nucleation resistance and potential nobility of pitting corrosion resistance. The nobility potential value of pitting resistance was reduced gradually due to the temperature of sensitization increase from 500 to 900 ºC. It can be concluded that the passivity would be destroyed and pitting corrosion resistance were decreased due to the present of carbides precipitation

Image analysis program is used to display the chromium carbides after heating the specimens of AISI 304 stainless steel. Figure (2) shows the carbides distribution and their amount in the microstructure of austenitic stainless steel after heating at different temperatures. Figure (8) shows that as heating temperature increase, the carbides increased also. Thus will be increasing the pitting corrosion as shown in the Fig. (9). The tendency to pitting corrosion increases with increases heating temperature. This can be explaining by plotting the relationships between heating temperatures and pitting potential as shown in Fig. (10). As the pitting potential decreases the pitting corrosion take place early.

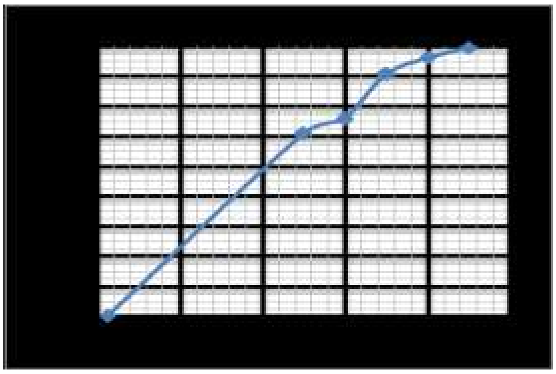


Figure 8: The relationship between Sensitization temperature and carbides precipitation

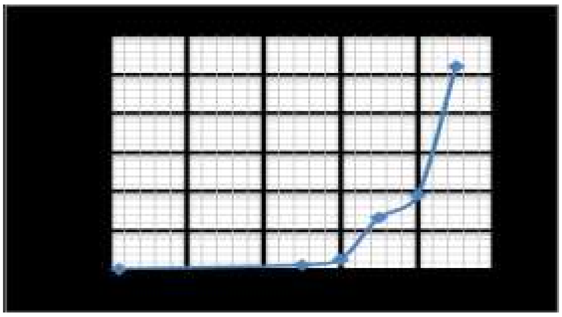


Figure 9: The relationship between Sensitization temperature and i_{pit}

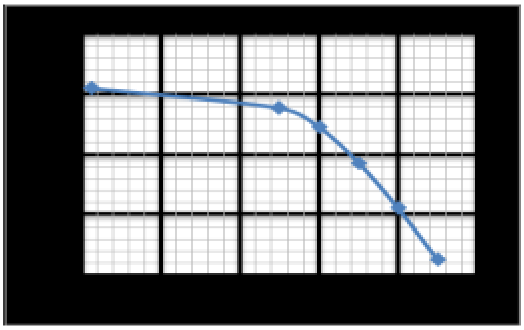


Figure 10: The relationship between Sensitization temperature and E_{pit}

In order to Prediction the initiation of pitting corrosion depending on carbides in the microstructure of 304 stainless steel the following equation is found to show the role of carbide in forming pitting corrosion.

f(x) = -3.395*x^4 + 19.03*x^3 + -36.79 *x^2 + 32.44 *x + 1.562

x= log(I)

(with 95% confidence bounds)

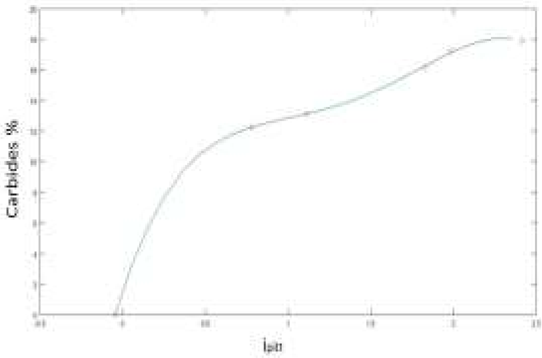


Figure 11: Pitting corrosion as a function of carbides percentage

Were F represent amount of carbides precipitation in the microstructure, when X represent pitting corrosion rate, P is steady value depended on metal type and can be extracted from drawn the relationship between pitting corrosion density and amount of carbides.

On this study have been take P value

The curve in the above figure refers to increase the pitting corrosion density with increase carbides amount. This results because the galvanic effect between carbides and the matrix. From this equation in fig. (11) Can be calculated the pitting corrosion density depended on percentage of carbides precipitation on the grain boundary.

4. Conclusions

1-As heating temperatures increase the chromium carbides will be more precipitated at grain boundaries.

2-As carbides increase , pitting corrosion occurs easily due to appear chromium depletion zones in addition of galvanic effect between carbides and matrix.

3-To achieve the aims of this work the following equation have been obtained

a- Mathematic equation had found to relate the initiation of pitting corrosion and chromium carbides as follows;

f(x) = -3.395*x^4 + 19.03*x^3 + -36.79 *x^2 + 32.44 *x + 1.562

x= log(I)

b- Mathematic equation had found between the number of pits and carbides percentage as follows;

y = 0.15786*x^3 + -3.8319*x^2 + 44.202*x + 97.935

c- Mathematic equation had found between the size of pits and carbides percentage as follows;

y = 0.0021697*x^3 + -0.029479*x^2 +0.22958*x + 0.2978

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