Corrosion and Electrochemical Behavior of Martensitic-Austenitic Stainless Steel in Hydrochloric Acid Solutions

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ABSTRACT: Corrosion and Electrochemical behavior of martensitic-austenitic stainless steel was investigated in 0.5,1,3 and 5wt. % HCl solutions by weight loss and electrochemical methods. The results indicated that the increase of acid concentration shifts the corrosion potential to more negative values and increasing the corrosion current. Also the results showed that this steel has a passive region in 0.5 and 1 wt. % HCl while the passivity disappeared completely in 3 and 5wt. % HCl. On the other hand the morphology of surface after corrosion tests indicated that this type of steel suffers from pitting corrosion.

Keywords: Martensitic-austenitic steel, potentiodynamic polarization, passive region

INTRODUCTION

Martensitic stainless steels are commonly used for manufacturing components with high mechanical properties operating under conditions of either high or low temperature. As their properties can be changed by heat treatment, these steels are suitable for a wide range of applications such as steam generators, pressure vessels, cutting tools, and offshore platforms for oil extraction [1–3]. An increase in the nickel content increases toughness and leads to the martensitic-austenitic steels. These are characterized by high strength, good high temperature strength and, because of the low carbon content in the martensite, good toughness even when welded [4].

Martensitic-austenitic Stainless steel is resistant to corrosion due to the formation of a passive film; however, localized corrosion can occur in the presence of aggressive anionic species. Chloride ions (Cl)) are usually, although not always, the main cause. The aggressiveness of the Cl) is due to its small size, high diffusivity and strong acidic anionic nature [5]. However, there is a poor literature on the corrosion behavior of this steel in corrosive acid environment [6] therefore the objective of this study is to investigate corrosion and electrochemical behavior of martensitic-austenitic stainless steel (10X17H3Γ6, GOST standard) in hydrochloric acid solutions.

EXPERIMENTAL WORK

Material

The present study was carried out using commercial austenitic stainless steel. Its chemical composition was analyzed by X-ray fluorescence and is shown in Table 1.

Table 1
Chemical Composition (wt %) of the Investigated Alloy

C	Cr	Ni	Mn	Si	S	P	Ti	Fe
0.106	16.274	3.012	6.082	0.662	0.008	0.03	0.252	balance

Weight Loss Experiment

Standard weight loss tests were carried out under the procedure according to ASTM G31 [7]. Specimens were cut into 5mm×5mm×25mm coupons for immersion tests and three coupons were used for each acid concentration. Before exposure, the samples were mechanically polished using wet SiC paper (initially 400, 500,800 and 1200 grades(and lubricated using distilled water. The polished samples were cleaned with acetone, washed using distilled water, dried in air and

stored over a desiccant. The samples were weighed before exposure by means of an analytical balance with a precision of 0.00001 g for the original weight (W0) and then hung in test solutions for 5 hr. After immersion at these times the corroded specimens were removed from the solutions, cleaned with distilled water and dried. Finally, the coupons were weighed again in order to obtain the final weight (W1).

Electrochemical Technique

Polarization tests were carried out in Potentiostat-model (PI-50-1). The specimens were polished to 1200 grit sizes and then cleaned with distilled water. Prior to electrochemical tests, the specimens were cathodically cleaned for 15 min at -0.60 V Ag/AgCl to remove the air-formed oxide film. A three-electrode cell composed of a specimen as a working electrode, Pt counter electrode, and Ag/AgCl reference electrode were used for the tests. Polarization tests were carried out at a scan rate of 12 mV/min at 25 °C. Specimens with exposed surface area of 0.30 cm^2 were used as a working electrode. The surface morphology before and after the corrosion tests was examined by metallurgical microscope model PME Olympus.

The solutions were prepared using analytical reagent grade chemicals and double distilled water. The volume of the test solution was 250 ml. The temperature of the test solution was maintained thermostatically with an accuracy of ±1 °C.

RESULTS AND DISCUSSIONS

Dissolution speed of martensitic-austenitic stainless steel in different hydrochloric acid concentrations was studied by weight loss method. Figure 1 shows that with increasing hydrochloric acid concentrations, the dissolution speed increases. This explains the fact that increasing acid concentration, both acidity and Cl$^-$ ion concentration increase. It is known that Cl$^-$ ion has small size, high diffusivity and strong acidic anionic nature therefore the electrochemical reaction increases by increasing acid concentration. The calculated corrosion rates against concentrations are shown in Figure 2. The corrosion rates can be correlated with the acid concentration by the following equation:

$$\log ????\log k ??B\log C_{HCl} \qquad (1)$$

Where:

k - the specific reaction rate constant;

B- the reaction constant;

C_{HCl} - the concentration of HCl solution.

K value represents the corrosion rate when the concentration of acid is equal to unity. The estimated B and k values are 2.234 and 5.4*10^{-2} mg cm^{-2} h^{-1}, respectively.
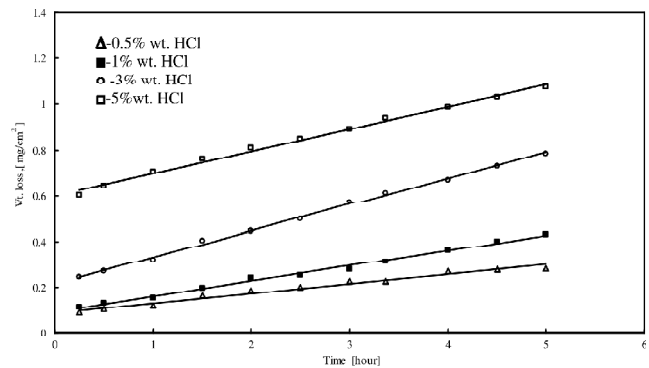

Figure 1: Weight Loss-time Curves for the Corrosion of Martensitic-austenitic Stainless Steel in Hydrochloric Acid Solutions
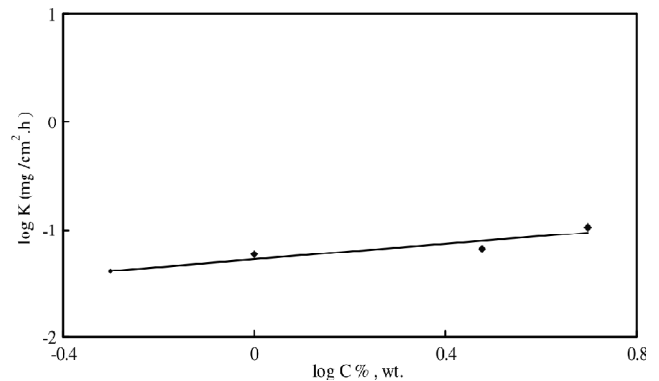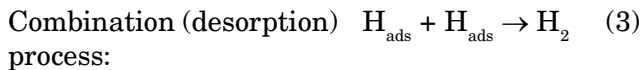

Figure 2: Plot of log K as function in log C$_{HCl}$ %

Figure 3 shows plot of open circuit potential (OCP), versus immersion time for martensitic-austenitic stainless steel. It is indicated that increasing the hydrochloric acid concentration from 0.5wt. % to 5 wt. % the open circuit potential (OCP) shifts to the negative side. This means that increasing the concentration of hydrochloric acid solution weakens the oxide film on the surface of steel and increases the electrochemical reaction [1].

Figure 4 shows the potentiodynamic polarization curves of martensitic-austenitic stainless steel in hydrochloric acid solutions. The cathodic polarization curves show a regular pattern and the current densities of the cathodic reaction increases with increasing the

concentration. The cathodic curves are also associated with hydrogen evolution. Li [8] and Ehteram [9] indicated that hydrogen atoms produced by the following cathodic reactions on the electrode surface:

Ionic reduction: $\qquad H^+ + e \rightarrow H_{ads}$ (2)

Combination (desorption) process: $\quad H_{ads} + H_{ads} \rightarrow H_2$ (3)

And/or: $\qquad\qquad\quad H_{ads} + H^+ + e \rightarrow H_2$ (4)

H_{ads} is the adsorbed hydrogen atom on the electrode surface and represents an intermediate state prior to desorption or diffusion into the metal. One of the combination steps (Eq. (3) or Eq. (4)) predominates depending strongly on the cathodic current density or overpotential. During polarization, the ionization is a possible way for H_{ads} atoms in addition to the desorption as H_2 and the absorption as hydrogen atom (H_{abs}) in the metal. H_{abs} atoms may also undergo oxidation. In addition, both the reducing pretreatment and the determination of cathodic polarization curve produced some hydrogen atoms as H_{ads} and H_{abs} on the electrode surface [8].
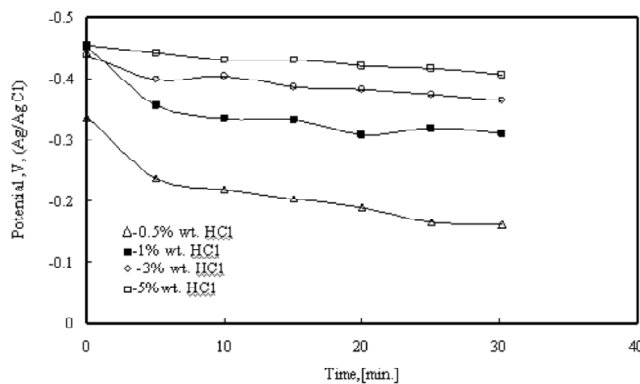

Figure 3: Variation of Corrosion Potential with Time for Martensitic-austenitic Stainless Steel in Hydrochloric Acid Solutions
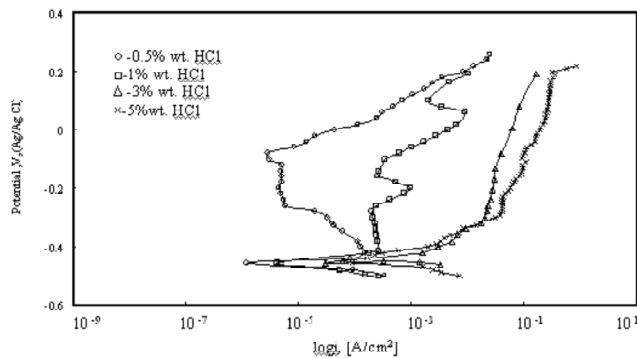

Figure 4: Effect of Hydrochloric Acid Concentration on the Cathodic-anodic behavior of Martensitic-austenitic Stainless Steel

On the other hand anodic polarization curves show that with an increase in hydrochloric acid concentration from 0.5 to 5%wt. the corrosion potential (E_{cor}) shifted to more active potential regions and the corrosion current density (i_{corr}) increased significantly. Also anodic polarization curves show that martensitic-austenitic stainless steel has passive regions in 0.5 and 1%wt. HCl solutions while the passivity disappeared completely in 3 and 5wt. % HCl. This behavior is attributed to the aggressiveness of the Cl⁻ ions which destroys the oxide film on the surface of steel [5].

The corrosion parameters of martensitic-austenitic stainless steel in hydrochloric acid solutions can be shown in Table 2.

The linear relation between $E_{corr.}$ and log C_{HCl} is illustrated in Figure 5 and can be given by the following equation:

$$E_{cor} = E^\circ_{cor} + a \log C_{HCl}$$ (5)

where $E^\circ_{cor.}$ is the corrosion potential when the acid concentration equal to unity The estimated value of $E^\circ_{cor.}$ is about -0.42V which is similar to that recorded in Table 2 for martensit ic-austenitic stainless steel sample in 1.0 wt.% HCl. at 25°C

The morphology of surface before and after corrosion test in 5% HCl for 3 hours is shown in Figures 6 and 7, indicated that this type of steel suffers from general corrosion and selective attack which produces pitting.
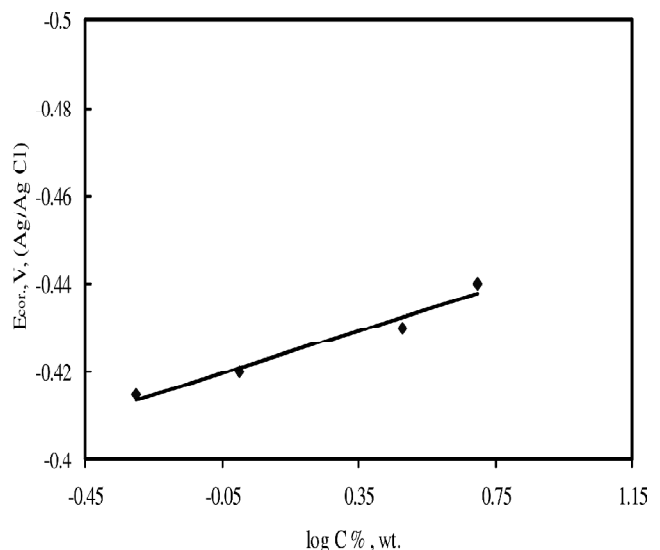

Figure 5: Plot of $E_{cor.}$ as Function in log C_{HCl} %

Table 2
The Corrosion Parameters of Martensitic-austenitic Stainless Steel in Hydrochloric Acid Solutions

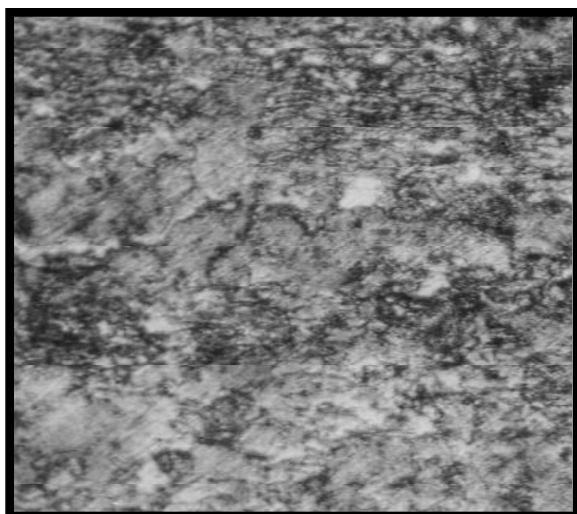| Conce. Wt %	$E_{cor.}$ (V)	E_p (V)	I_{cor} (A/cm²)	I_p (A/cm²)	b_c	b_a
0.5	-0.415	-0.260	$8.2*10^{-5}$	$6.03*10^{-6}$	-0.016	+0.018
1	-0.420	-0.415	$4.17*10^{-4}$	$2.6*10^{-4}$	-0.027	+0.025
3	-0.430	——	$7.02*10^{-4}$	——	-0.021	+0.023
5	-0.440	——	$9.09*10^{-4}$	——	-0.026	+0.035

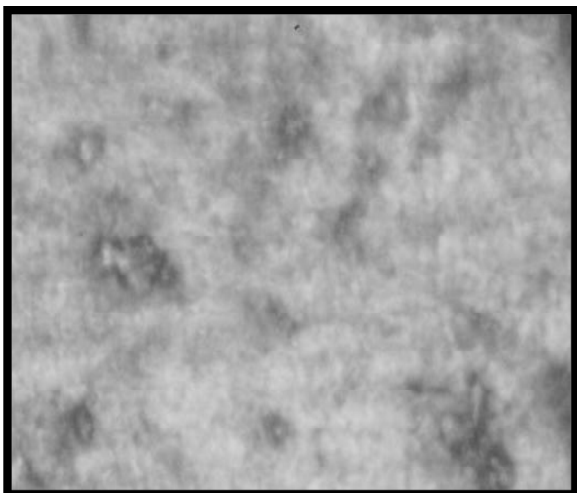**Figure 6:** Morphology of Surface before Corrosion Test (X200)

Figure 7: Morphology of Surface after Corrosion test in 5% HCl for 3 hours (X200)

CONCLUSIONS

This study investigated the hydrochloric acid concentration on the corrosion resistance of martensitic-austenitic stainless steel. The results show that:

1-An increase in hydrochloric acid concentration increased the susceptibility to active dissolution and decreasing passive region.

2-The passivity disappeared completely in 3 and 5wt. % HCl.

3-Microstructural studies for this type of stainless steel after immersion in HCl solution showed that this type of steel suffers from general and pitting corrosion in hydrochloric acid solution.

References

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