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Electrochemical Behavior of Maraging Steel in Chloride Containing Environment

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Electrochemical behavior of aged and solution treated maraging steel have been investigated, in NaCl using open circuit potential (OCP) and potentiodynamics measurements. OCP shifts to more noble value during initial stage of immersion followed by slow shift in potential during the middle stage of immersion and eventually attain a steady state of potential during the last stage of monitoring. Various properties, such as, mechanical properties and corrosion resistance were investigated for aged and solution treated steel. Aging the maraging steel improving the mechanical properties and enhances the corrosion process. Maraging steel exhibits better passivity during polarization at low NaCl concentration and the passive region is broader than at higher concentration.

Keywords: Maraging steel, polarization, open circuit potential, tensile properties

1. INTRODUCTION

Maraging steels are a class of ultra-high strength steels developed mainly for aerospace, military, aircraft and tooling applications. The high strength of maraging steel is achieved by aging the specimen at 400- 500 °C, where the precipitation of intermetallics takes place [1]. Strengthening is achieved by the use of substitutional alloying additions that result in the precipitation of secondary phases during age hardening of a quenched martensitic iron–nickel matrix. The development of maraging steels started on steels containing 20 and 25% Ni using a combination of aluminum, titanium, and niobium as age-hardening elements.[2] . Further work [3] was conducted and indicated the important synergistic age-hardening effect of cobalt plus molybdenum and eventually led to the development of the 18% Ni maraging steels. Maraging steels are characterized with high ductility, formability, corrosion resistance, high temperature strength and ease of fabrication, weldability and maintenance of invariable size even after heat treatment [4].

Effect of addition of alloying elements on the grain boundary brittleness of Fe–Ni–Mn maraging steels has been investigated extensively [5–9]. Corrosion of maraging steel has received a considerable amount of attention. It undergoes more or less uniform corrosion and gets completely covered with rust [10] when exposed to atmosphere. Maraging steels are found to be less susceptible to hydrogen embrittlement than high-strength steels owing to significantly low diffusion of hydrogen [11]. It was reported previously that the corrosion of maraging steel in slightly acidic radioactive water in the absence and presence of chloride ions, depended on pH, and the intermediates remained on the maraging steel surface in the active region, favoring the passivity [12]. The effect of carbonate ions in slightly alkaline medium on the corrosion of maraging steel was studied by Bellanger [13]. A previous study indicated that aged maraging steel substantially corroded in phosphoric acid medium [14]. Recently, the corrosion behavior and hydrogen evolution reaction of weld aged maraging steel have been investigated, in 1.0 M sulfuric acid solution containing different concentrations of 2-(4-chlorophenyl)-2-oxoethyl benzoate (CPOB). The data obtained from polarization technique showed that the corrosion current density and the hydrogen evolution rate decrease with increasing the inhibitor concentration [15].In the present investigation, the electrochemical behavior of Maraging steel will be investigated at different NaCl concentrations. Various properties, such as, tensile properties and corrosion resistance will be also evaluated. These properties are examined with the measurements of electrochemical technique and tensile test on the aged and solution treated steel.

2. EXPERIMENTAL

2.1Material

Table 1. Chemical composition of maraging steel

C	**0.0497**
Si	**0.253**
Mn	**0.398**
P	**0.0274**
S	**0.0203**
Cr	**5.43**
Mo	**4.48**
Ni	**12.64**
Al	**0.125**
Ti	**0.003**

Table (1) illustrates the chemical compositions of the maraging steel samples. The working electrode was cut from the sample and sealed with epoxy resin, leaving only 0.8 cm^2 of the surface area exposed to the electrolyte. Prior to each experiment, the working electrode was mechanically polished with a fine grade of emery papers (400-2000 grade). Then it was degreased with acetone, washed with double distilled water and dried before immersing in the corrosion medium. Maraging steel specimens are aged at 450 ^oC and solution treated at 820 °C for 1 h. All the experiments were carried out at temperature 25 ^oC.

2.2. Electrochemical Measurement

Electrochemical measurements were carried out using potentiostat model IM6e (Zahner Elektrik). The arrangement cell used was a conventional Three-electrode compartment glass cell was used through the whole experiments. A platinum electrode and a saturated calomel electrode (SCE) were used as counter and reference electrode, respectively. All the values of potential are referred to the SCE. The polarization studies were carried out at scan rate of 1 mV s^{-1}.

2.3. Test solution

The test solution was NaCl solution prepared from analytical-reagent-grade reagent NaCl and double distilled water. The concentration range of NaCl used in this study was 0.6 - 2 M .

3. RESULTS AND DISCUSSION

3.1. Open Circuit Potential (OCP) measurements

Figures 1- 3 show the monitoring data of the open circuit potentials of steel electrode with immersion time in NaCl solution with different concentrations (0.1, 0.6 and 2M). The change in the potential upon immersion in solution indicates the nature of reaction taking place on the surface. The open circuit potentials of the maraging steel have a tendency to shift towards more noble values in 0.1 and 0.6M NaCl solutions. On the other hand, the open circuit potentials of the sample changing towards less noble values immediately on immersion in 2M NaCl solution. The monitoring data displayed in figures 1-3 can be classified in three distinct regions as shown in Fig. 4. In Case of 0.1M and 0.06 M NaCl solution, OCP rapidly shifts towards more noble values (curve A) during the initial stage of immersion as shown in region I, which can be accounted to a rapid passive film formation. There are two processes occurring during the immersion of the maraging steel in NaCl solution. The first process is the passive film formation and the second one is the passive film dissolution. The slow shift in potential during the middle stage of immersion (region II) was attributed to the competing processes occurred between the film formation and dissolution. The former process is predominant process inside region II and causes a slow shift in the potential towards more noble values. The steady state potential observed during the last sage of monitoring (region III) can be attributed to the equal processes of the film formation and dissolution, which leads to steady state. This explanation is based on the idea that the potential is determined by a simultaneous passive film formation (determining step) and dissolution, in which the anodic reaction is the film growth rate.

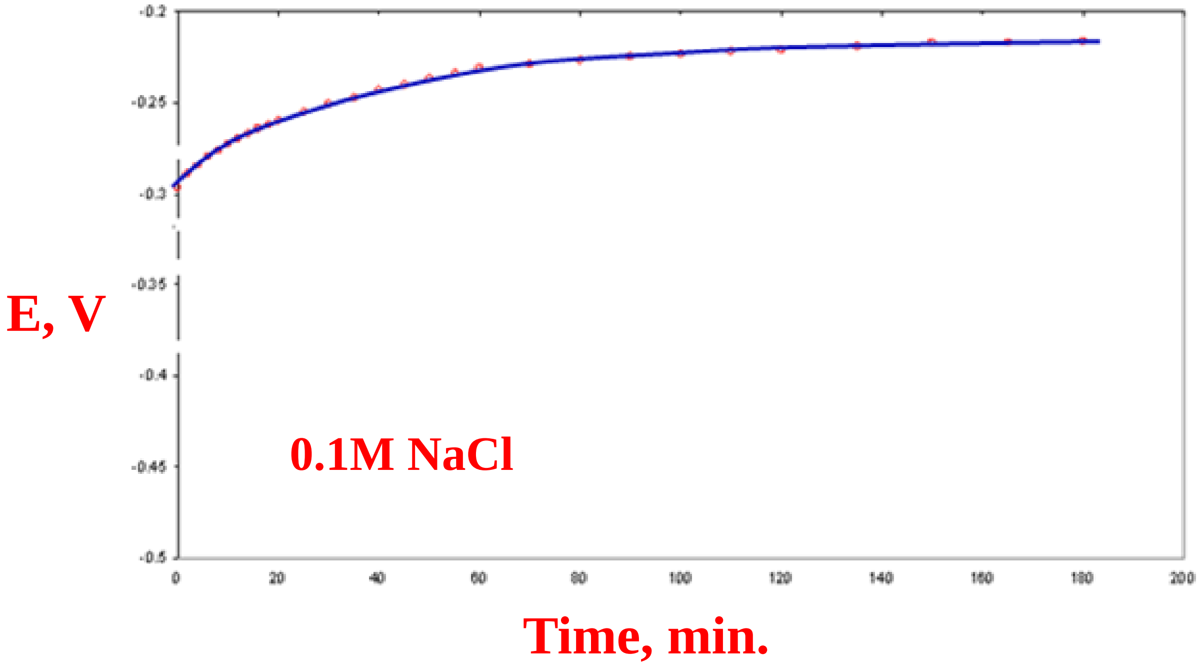

Figure 1. Variation of potential with immersion time for maraging steel immersed in 0.1M NaCl solution.

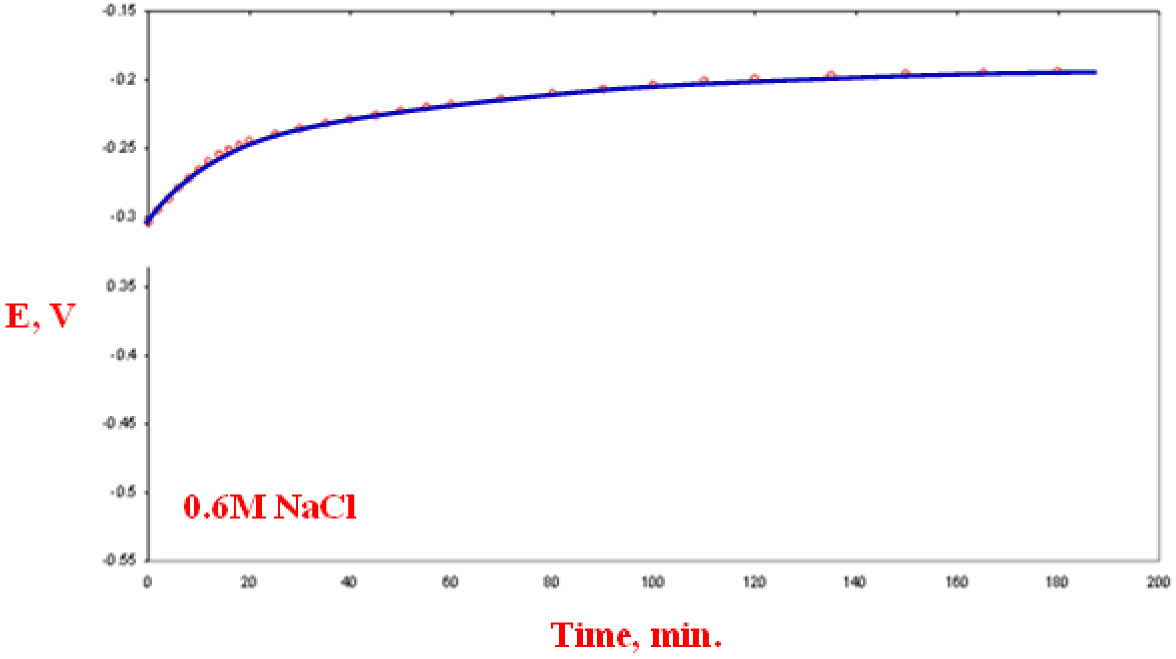

Figure 2. Variation of potential with immersion time for maraging steel immersed in 0.6M NaCl solution.

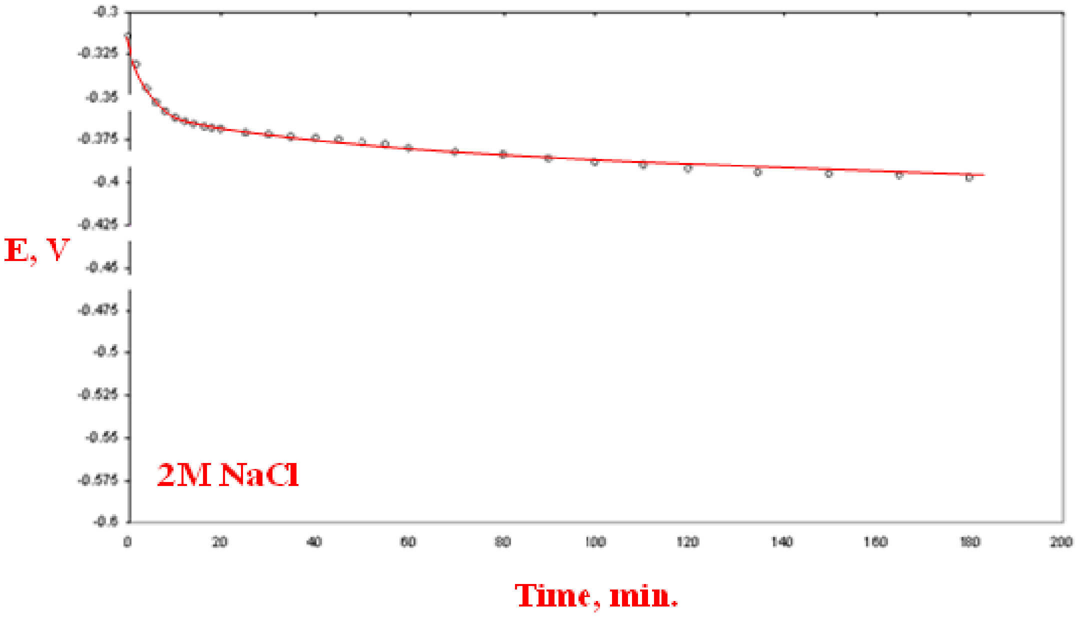

Figure 3. Variation of potential with immersion time for maraging steel immersed in 2M NaCl solution.

The presence of Cl ion in solution initiates breakdown of passive film and the reaction is diffusion controlled. With increasing chloride ion concentrations, the diffusion of the ions disappear and the interfacial reactions become charge transfer controlled, so that the tendency for steel to corrode in solutions increases with increasing NaCl concentration 2M (16).

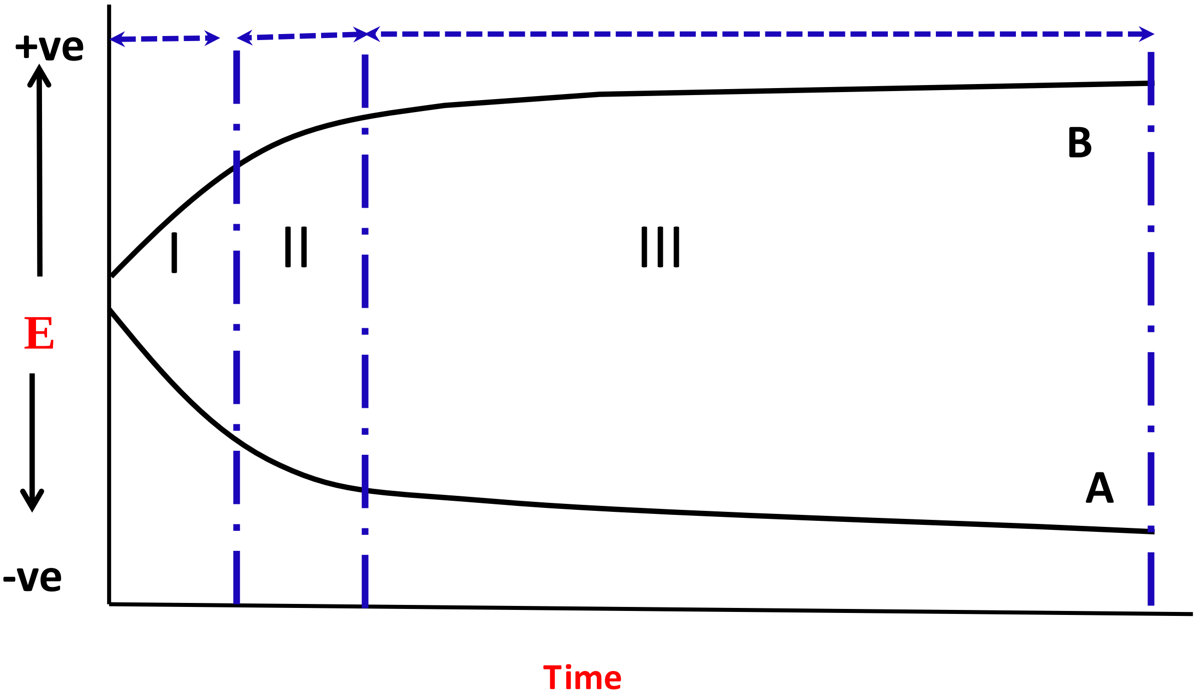

Figure 4. Schematic diagram for explanation of monitoring data of potential with time.

The behavior of steel in 2M NaCl solution is entirely different from the behavior observed in 0.1 and 0.6M NaCl solution. This behavior can be explained by curve (B) as shown in Fig. 4. The rapid shift in potential towards a less noble direction during the initial stage of immersion (region I) can be attributed to the rapid dissolution of the steel, while the surface is bare. The dissolution process increases as immersion time progresses. The dissolution rate of passive film decreases slowly during the middle stage of monitoring owing to the competing processes between the passive film growth and the dissolution. The latter process is a predominating process. The steady state observed during the last stage of immersion in region III could be attributed to the equal process of passive film formation and dissolution. The film thickening rate increased gradually in with increasing the concentration of NaCl concentration of 0.1M and 0.6M. This may be explained by assuming that the adsorption of these ions promote the development of thicker passive film. In case of 2M NaCl solution the film starts to dissolve followed by the dissolution of the underlying surface. As shown in Table 1, the steel sample contains molybdenum content (*4.48%*), which enhances the tendency of the steel sample to form passive film, which protecting the underlying surface and causes a shift in potential to more noble values.

3.2 Potentiodynamic polarization measurements

Potentiodynamic polarization curves for the maraging steel in NaCl solution with different concentrations (0.1-2M) are shown in Figs. 5-7. The polarization data exhibits a passive region and causes a shift in potential to noble value with decreasing NaCl concentration. The data also show plateau, which indicates the ability of surface to form a passive film.

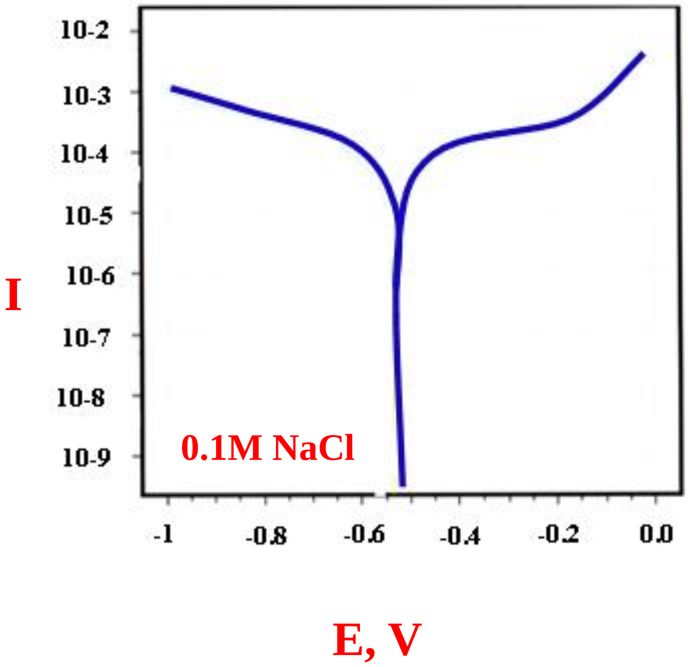

Figure 5. Polarization curve for the corrosion of maraging steel in 0.1M NaCl solution.

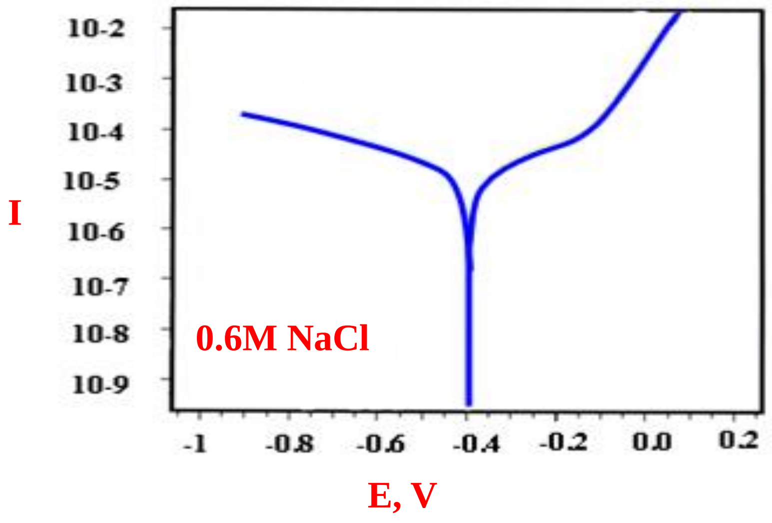

Figure 6. Polarization curve for the corrosion of maraging steel in 0.6M NaCl solution.

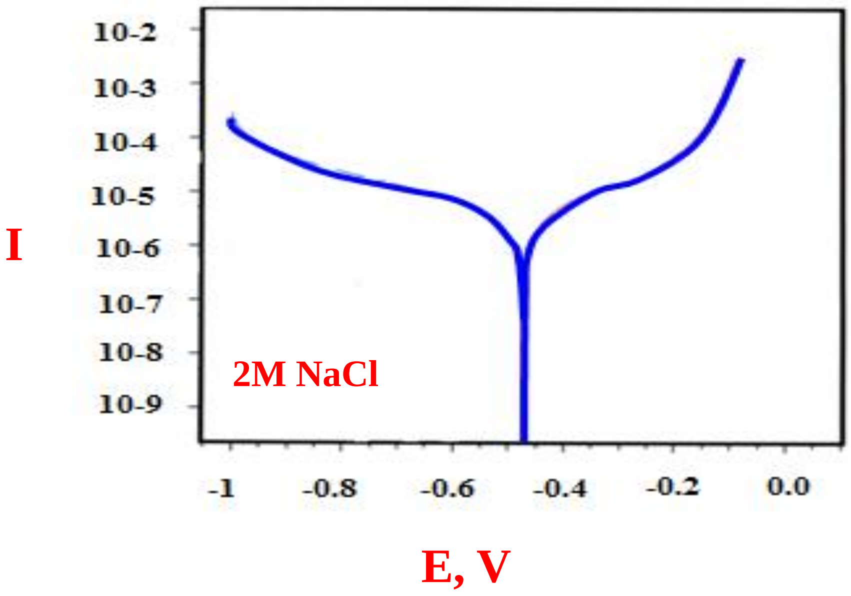

Figure 7. Polarization curve for the corrosion of maraging steel in 2M NaCl solution.

The passive region was limited by the breakdown potential, which corresponds to a rupture of the passive film on the surface. The length of passive region decreases with increasing NaCl concentration. This accompanied by a rapid increase in the current density at the end of polarization measurement. This is can be explained on the basis of the aggressive nature of the chloride ion, which causes a rapture of the passive film. It is clear that the cathodic branches exhibit a Tafel behavior denoting that the cathodic hydrogen evolution reaction on the steel surface is under activation control. Hydrogen evolution has been reported to be generally the dominant local cathodic process in the corrosion of carbon steel in acidic aqueous solution [17-18] solutions via hydrogen ion reduction.

3.3 Effect of aging on the Mechanical properties

On heat treating at 485 °C, a very rapid age hardening reaction takes place and greatly strengthens the material. Maraging steels transform completely to martensite on cooling to room temperature after annealing The annealed structure consists of packets of parallel lathlike martensite platelets arranged within a network of austenite grain boundaries. Aging for several hours at 485 °C results in a Ni_3Mo phase, while longer times produce the Fe_2Mo phase. . The addition of chromium on maraging steels augments the precipitation of Ni_3Ti and Fe_2Mo intermetallics and indirectly reduces manganese segregation at grain boundaries [19]. The weak segregation of chromium at iron grain boundaries reduces grain boundary cohesion of iron according to a pair bonding theory [20-21]. Hossein Nedjad et al. [21-22] proposed a mechanism for grain boundary embrittlement of Fe–Ni–Mn maraging alloys in which discontinuous coarsening of grain boundary precipitates in association with inhomogeneous planar slip, which have been considered as a main source of intergranular brittleness. Tensile properties for the solution treated and aged samples are given in Table 2.

Table 2. Mechanical properties of Maraging steel before and after aging

Mechanical Properties	Aging	Test sample
Yield Strength	Before	890
	After	1427
Ultimate tensile strength	Before	1092
	After	1429
Elongation (A) %	Before	14
	After	12

Aged specimen exhibits an increase in ultimate tensile strength (UTS) and yield strength (YS) and a decrease in percentage elongation to fracture (%El). The higher values of UTS and YS and lower values of %El exhibited by aged sample can be attributed to the hardening of the surface. For solution-treated specimen, the grain boundary acted as a barrier for dislocation movement during tensile loading. Therefore, the coarse-grained specimen (with fewer grain boundaries) had lower yield strength than the aged specimen

3.4 Effect of aging on the electrochemical behavior

Fig.8 shows the influence of aging on the electrochemical behavior of maraging steel. It can be seen that the solution-treated specimens were quite resistant to corrosion and exhibited a passive region. The sharp increase in current density observed during the end of passive region was attributed to the breakdown of the passive film. The difference in susceptibility to corrosion can be accounted to the different in microstructure of the aged and solution treated specimen. The results indicated that the aged specimens comprised of numerous precipitates led to a raised Capp and causes an increase in the susceptibility to corrosion as compared to those of the solution-treated ones.

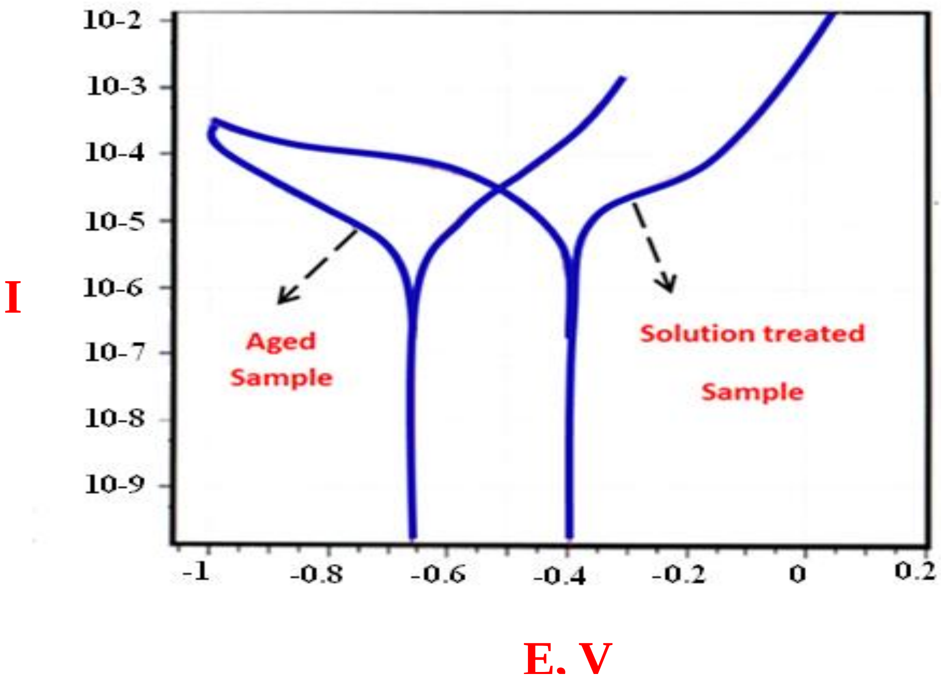

Figure 8. Polarization curves for the corrosion of aged and solution treated maraging steel in 0.6M NaCl solution.

The solution-treated specimens were resistant to corrosion, whereas aged specimens were susceptible to it, implying the strength level was the controlling factor to affect the corrosion susceptibility of the specimens. The high corrosion resistance of the solution-treated specimen was attributed to their inherent high ductility. Additionally, increasing the grain boundary area by reducing the grain size also contributed somewhat to enhance corrosion process in the aged - treated specimen. As a result, the coarse-grained of the aged specimens facilitated the fractures of the specimens in NaCl and consequently enhances the corrosion process. For solution-treated specimens, the tendency to form a passive layer increased and exhibited more resistance to corrosion process. Moreover, aging the specimens is responsible for the grain boundary embrittlement [23-24] , which in turn enhances the corrosion process. It was reported previously that the age hardenability has been found to suffer from premature intergranular brittleness after aging treatment (25), which in turn reduce the corrosion protectiveness of the steel.

4. CONCLUSIONS

1- Aging of Marging steel substantially improves the mechanical properties of the steel.

2- The aged specimens were susceptible to corrosion process than that experienced by the solution-treated specimens.

3- Open circuit potential shifts to more noble value during initial stage of immersion followed by slow shift in potential during the middle stage of immersion and eventually attain a steady stat of potential during the last stage of monitoring.

4- Maraging steel exhibits better passivity during polarization at low NaCl concentration and the passive region is broader than at higher concentration.

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