

Study Corrosion of High-Mn Steels with Mo in 3.5% NaCl Solution.

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Abstract. TWIP steels are high Mn (17-35%) austenitic steels having strength and ductility concurrently. This makes them suitable for applications that need high strength and ductility like gas tanks and oil platforms. To these applications corrosion resistance of these steel is also of paramount importance and needs to be noticed. Alloying elements can affect corrosion behavior of the steels due to difference between electrochemical properties of them. As Mo is an effective element on corrosion resistance in marine atmospheres containing chloride ions, its effect on corrosion behavior of TWIP steel was investigated. This was achieved by two usual methods of weight loss and potentiodynamic polarization of the samples, after that they casted and hot rolled in experimental scale. The results showed enhancement of corrosion resistance and decrease of pitting of steel by adding Mo to its chemical composition.

Keywords: TWIP Steel, Pitting corrosion, Molybdenum, 3.5% NaCl Solution.

1. Introduction

TWIP steel has the advantages of high mechanical strength and high elongation rate simultaneously. It is employed in various applications like gas tanks and oil platforms. Although corrosion and its impacts on steels are vital and important matters no enough researches however, have been ever carried out for assessing these issues. The influence of alloys on steel properties is another important matter since alloys can change corrosion behavior of steels through altering their electrochemical properties. There are fewer literatures about the role of manganese and aluminum on corrosion behavior of Fe-Mn-Si-Al steels. [1]

Manganese is used for austenitizing microstructures of steels and lowering the amount of solved nitrogen. Adding manganese to steels usually leads to decreasing corrosion resistance of steels specially leads to formation of corrosion pits due to creation of manganese sulfide impurities, which are considered as locations for anions attacks [2] But studies of Stewart & Williams revealed that these impurities also serve as cores for creation of corrosion pits [3]. According to studies, adding 25% manganese to soft steels has decreased corrosion resistance of the steels against aqueous solutions [1]. The results of another study show that adding 5% aluminum improves corrosion resistance of Fe-25Mn steel against 3 kinds of solutions i.e. 50% nitric acid, 50% sodium hydroxide and 1 molar of sodium sulfate. [4]. Generally, the high corrosion resistance of austenite stain less steels has been ascribed to creation of passive oxide layers on surface of steels during their interaction with aqueous environments [5]. Environmental conditions and chemical composition of alloy define the strength of these passive layers. Also, it has been cleared that aggressive ions like chloride anions make corrosion pits on the surfaces subjected to corrosive environment through breaking passive layers and inhomogeneous regions [6].

We can divide pitting corrosion process into 3 consecutive stages. The primary stage, the meta stable propagation stage and stable propagation of pits [7]. In the primary stage the passive oxide is broken in the presence of aggressive ions. In the meta stable propagation stage, small pits are created but it is possible to them to repassivate automatically. This possibility is crossed out as the rate of corrosion increases and stable

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pits are created. Various theories have been proposed about the influence of molybdenum on steel properties. Generally, we can classify them into 2 categories. 1) Molybdenum changes the polarity of passive film through crating molybdates and creates bipolar layer and 2) it improves repassivation behavior or deactivates pits growth. [8]

In this paper we try to have a good understanding of the influence of molybdenum on high manganese steels and their corrosion resistance properties and also creation of pits on their surfaces in a simulated environment of 3.5% sodium chloride.

2. Materials and Method

2.1. Preparing Samples and Their Chemical Composition

The steel was cast in induced furnace under neutral atmosphere. Table 1 shows its chemical composition. Then we carried out normalizing treatment for an hour at 1200°C in order to prevent the segregation of alloy elements especially manganese from grain boundaries. Then the steel was hot rolled in 5 consecutive pass in order to apply the real strain of 70% on it and then it was cooled in air. The ultimate rolling temperature was 900°C. We tried to fix the percentage of manganese in order to study the impacts of molybdenum on this kind of steels.

Table 1: chemical composition of the steel (weight percent)

Steel	C	Mn	Si	Al	Mo	Fe	S
1	0.13	32.9	3	2	-	Bal.	<0.06
2	0.13	33	3	1.9	0.3	Bal.	<0.06
3	0.13	33	3	2	1.3	Bal.	<0.06

2.2. Weight loss measurements

In order to fulfill corrosion test we used weight loss and polarization methods. For weight loss method we prepared samples with 20×10×3 dimensions. Then we washed them in 98% ethanol and weighted and finally tested them. In order to measure the weights of samples we used digital scale with 0.001 mg accuracy. Also, we carried out immersion test in accordance with ASTM G31-72. During test, the temperature of solution was fixed at 23±1 centigrade degree. We used 3.5% sodium chloride solution for this test. In order to gather more information about corrosion behaviors of the samples, we measured samples after 50, 100, 200 and 300 hours and calculated weight loss through following equation:

$$M_u = \frac{M_p - M_k}{A} \quad (1)$$

In which M_p is the initial mass of samples, M_k is the mass of samples after test and A is the surface subjected to corrosive environment. Also, we calculated corrosion rate by following equation:

$$V_{cor} = \frac{\Delta m}{S \cdot t} \quad (2)$$

In which S is the surface of samples (mm^2), t is measuring time (hour) and m is the lost weight (mg).

2.3. Electrochemical Measurements

Polarization test was carried out using an Autolab Pgstat 30 device. This device used calomel electrode as standard electrode, graphite as auxiliary electrode and the sample as work electrode. Scanning rate was 0.5mV/Sec during polarization. We placed the samples in electrolyte solution for half an hour in order to equilibrate samples with solution. Also, all samples were tested separately in 3.5% sodium chloride solution. The temperature of solution was considered the same as ambient temperature. After test, the samples were washed in distilled water and Aston via ultrasonic manner.

2.4. Estimations of Phases, Microstructures and Morphology of Surfaces

For microstructure study purposes the samples were prepared in accordance with ASTM E3-01 and ISO 4499. The samples were studied using a light microscope- model Olympus CK40M. For surface studies and also estimations of chemical composition of surface through EDS chemical composition analyze, we used a

SEM microscope (made in Czech Republic). Phase analyses of samples were carried out at ambient temperature through X-ray diffraction method using a Bruker device (made in Germany) in the angles ranged from 35 to 100 degree and $K\alpha_{Cu}$ ray and nickel filter.

3. Results and Discussions

Fig. 1 shows images captured by the light microscope from surfaces of samples before test. We can see annealing twins in microstructure of all samples. Also, the grain sizes have been decreased by increasing the level of molybdenum up to 3%. Our investigations show that the molybdenum prevents grain growth to some extent [9]. Also, the results of XRD indicate that although molybdenum is a ferrite making element but this is austenite which is the dominant phase in microstructures.

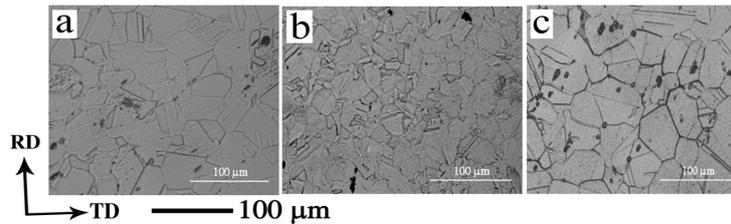


Fig. 1: microstructure of hot rolled samples. a) No Mo; b) 0.3% Mo; c) 1.3% Mo.

Fig. 2-a shows the graph of weight loss variations of samples immersed in 3.5% sodium chloride solution. Since this solution contains aggressive ions all samples have been corroded and we can see corrosion pits on surfaces. Of course there are apparent differences between samples with and without molybdenum element. Based on Fig. 2-a, we can find that by increasing the percentage of molybdenum in alloy steel, the slope of weight loss line versus corrosion time has been decreased. This implies that the corrosion rate has been decreased due to existence of molybdenum in alloy steel. Using the obtained weight loss, corrosion rates of samples have been calculated through the mentioned equation. The results have been shown in graph form in Fig. 2-c. This graph proves that the rate of corrosion decreases as the percentage of molybdenum in manganese steel increases. In order to identify the influence of molybdenum on corrosion resistance of samples we carried out potentiodynamic polarization test in 3.5% sodium chloride solution. Fig. 2-b shows polarization graphs. As we can see in the graphs adding molybdenum to alloy steel and increasing its percentage, causes the corrosion potential, E_{corr} , to approach to a noble value. Also, we saw that the corrosion current, I_{corr} , had lower values indicating lower corrosion rate of samples. This phenomenon is very similar to the result of studies carried out by Hovarth and Uhlig indicating significant increase of pitting potential in Fe-Cr, Fe-Cr-N and Ni-Cr alloys [10] It should be noted that the increasing of pitting potential is reversed by decreasing temperature.

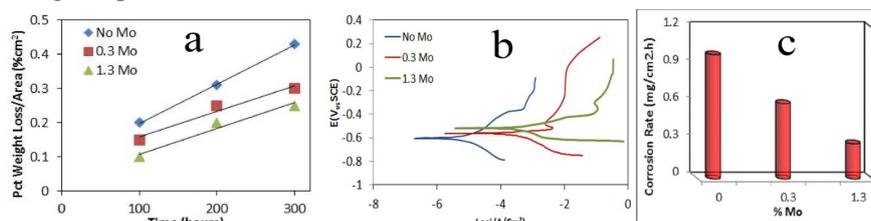


Fig 2: a) the results of weight loss test, b) polarization graphs of samples in 3.5% sodium chloride, c) variations of corrosion rate versus molybdenum percentage in alloy steels

As we expected, passive regions were formed in the samples subjected to corrosive environment. This implies formation of protective layers. [11] Table 2 shows the results of polarization investigations on samples.

Table 2: results obtained through analyzing polarization graphs

Steel	E_{Corr}	I_{Corr}
No Mo	-0.610	6.71E-5
0.3 Mo	-0.563	5.75E-5
1.3 Mo	-0.520	5.42E-5

As we mentioned above, the effects of manganese on corrosion resistance of steels have not been clearly identified yet. [12] Manganese tends to react with sulfur and form stable compound of MnS even in the presence of lower rates of sulfur. [13] Regions with MnS impurities are very appropriate zones for initializing corrosion process and formation of corrosion pits due to creation of anode regions on the surface of these zones. Under corrosive environment and anodizing condition the MnS impurities are unstable and tend to dissolve in network and impurities interface. Adding molybdenum in steels can increase corrosion resistance of steels and prevents formation of corrosion pits and their propagation through affecting on passive layers and repassivation process. Also, it is expected that the presence of molybdenum can prevent the raising of corrosion speed through forming MoO_3 oxide layers which convert to MoO_4^{2-} in the solution interface preventing flux of OH^- and Cl^- ions into films and pits. Fig. 3-a and Fig. 3-b shows images of the surfaces of samples captured by SEM microscope.

The results of recent studies show that during MnS dissolve, the level of Ph is decreased and under this acidic environment the molybdenum is solved quickly into alloy and forms oxides and protective layers. [10] Based on this phenomenon and according to Pourbaix diagram for molybdenum shown in Fig. 3-c, it seems that the dominant composition under PH=4 to 6 conditions is FeMoO_4 . With a probability bordering to certainty, this interaction is occurred near to metal's surface and within pits regions and we generally call them corrosion products.

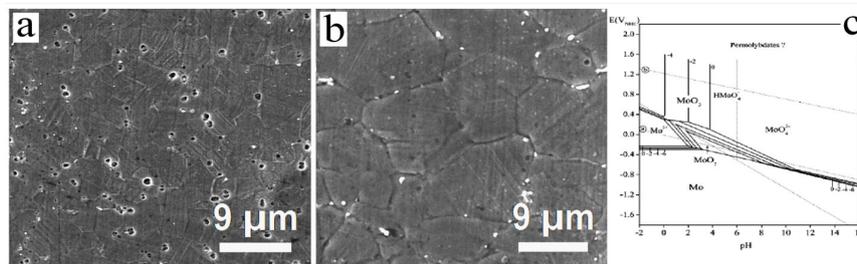


Fig. 3: Images of the surfaces of samples captured by SEM microscope for estimating the impacts of MnS impurities on samples purposes a) no Mo, b) 1.3% Mo, c) Pourbiax diagram for molybdenum at ambient temp

If PH drops to 2 to 4, then FeMoO_4 would be unstable within pits and in contrast MoO_3 would be a stable composition forming Molybdenum oxide on this region and prevents pits growth. For analyzing this hypothesis, we studied pits layout through EDS method and the obtained results emphasized the existence of the mentioned elements inside pits.

4. Result

- Pitting resistance of this steel decreases as the percentage of molybdenum increases. Also, corrosion rate decreases due to weight loss effects and the endurance and life of parts increases.
- MnS impurities which are electrochemically unstable and tend to dissolve form regions on surfaces which are susceptible to corrosion.
- Molybdenum affects various stages of corrosion process and decreases the attacks of aggressive ions.

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