



An Investigation on Corrosion and Stress Corrosion Cracking initiation of a Ferritic Stainless Steel in a Tertiary Amine Solution

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Received: 7 December 2018, Revised: 31 May 2019, Accepted: 4 September 2019
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Abstract

The present study focused on stress corrosion cracking (SCC) and corrosion behavior of ferritic stainless steel (grade 430) in activated methyl diethanolamine (aMDEA) solution, which is classified as a tertiary amine. In this regard, cyclic polarization and U-bend tests were performed in CO₂ loaded aMDEA with different concentrations at 25 and 70 °C to observe corrosion behavior and also the possibility of crack initiation. Based on the obtained results, it was found that the corrosion rate increased in concentrated amine solutions. Also, by increasing temperature from 25 to 70 °C both corrosion rate and susceptibility to SCC initiation were intensified. Increment of amine concentration and also increase in temperature led to more absorption of CO₂, generating a more acidic solution. Overall it could be stated that while for the grade 430 stainless steel investigated in this study corrosion and cracking was observed Therefore it could be concluded that in amine-containing environments this steel is not a very suitable alternative for carbon steels, which are commonly used in these environments.

Keywords:

aMDEA,
Corrosion,
Ferritic Stainless-Steel
Tertiary Amine Solution,
Stress Corrosion Cracking,

Introduction

Natural gas sweetening and CO₂ emission by alkanol amines first were submitted by Bottoms in the 1930s [1]. Nowadays alkanol amines are used in a variety of industries, including ammonia production, hydrogen production, gasification of extracted coal, gas synthesis for chemicals usage, ethylene manufacturing, and purification of natural gas [2].

The amounts of impurities in extracted natural gas are salient, which adversely affects all equipment that is facing natural gas. H₂S and CO₂ (called acidic gases) are recognized as two main contamination sources in natural gas processing [3]. Among all of the technologies used for purification of natural gas from acidic gas contaminations, alkanol amines are most popular nowadays. Alkanol amine process is efficient from the process point of view [4]. Although there are various types of amines, MDEA is preferred due to its lower costs and higher efficiency [3].

Amine solutions have some negative points, including the generation of unwanted combinations like special salts and compounds resulted from amine degradation [5]. Mentioned pollutants would lower the rate of acid gas absorption and increases the corrosion rate [6,7]. Amine solutions may not cause corrosion intrinsically, but they are eligible to become corrosive as a result of acid gas absorption or anions from amine degradation [4,8,9].

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From the 1950s, corrosion in gas sweetening plants which uses amine solutions was considered due to human, environmental and financial hazards [2,10-12]. Almost 25% of the maintenance budget for gas sweetening plants is being used for corrosion damages [13,14]. Most of the components degraded by corrosion in these plants are made from carbon steels.

Carbon steels are being used for plant construction and piping since they are low priced, accessible and easily manufactured [4,10]. However, usually, the hot spots in amine gas sweetening units are made of more heat/corrosion-resistant materials. In this regard usually, stainless steels are the first choice, due to their superior corrosion resistance.

Since ferritic grades have lower cost as compared to other grades (e.g. austenitic and duplex), it is worth investigating whether it could be used as an alternative for carbon steels in order to reduce the corrosion damages. In this regard, one of the most detrimental types of localized corrosion for stainless steel is stress corrosion cracking (SCC) [6,11,15]. Therefore, the objective of the present study is to investigate corrosion and SCC resistance of grade 430 stainless steel in activated Methyl Diethanol Amine (aMDEA) solution, at two different temperatures.

Materials and Methods

Grade 430 ferritic stainless steel with a three-millimeter thick sheet was supplied. In order to minimize carbides in the structure, solution annealing at 1050 °C was done for half an hour followed by water quench. Chemical analysis of the stainless steel sheets was done by Arun Spark Emission Spectrometer model PMI MASTER SMART. Tensile test was done by means of a Wolpert FM2750 tensile measuring machine. A Koopa pajoh UV1 test machine was used to measure the hardness of the samples. Phase identification of the heat-treated specimen was done by diffraction method (XRD) using a Philips Xpert MD, and results were analyzed by Xpert high score plus software.

For investigating the corrosion behavior of 430 stainless steel specimens in aMDEA solution, a cyclic polarization test was performed. Specimens with area 2cm² were cut from sheets, mounted in epoxy resin with insulated copper wire. Then polishing was performed up to No. 1200 by an emery paper. Corrosion tests were done in the same environment as the SCC tests. An IVIUMSTAT potentiostat was selected for cyclic polarization tests in three-electrode configuration corrosion cell. The reference electrode was Standard Saturated Calomel Electrode (SCE) and Platinum (Pt) as the counter electrode. The scanning rate was 0.5 mV/s for polarization tests. Specimens were kept in the aMDEA solution 1 hour prior to running each polarization test for reaching OCP condition.

In order to observe the SCC initiation process, constant load U-bend method was chosen based on ASTM G30-97. In this regard, sheets were first cut into proper dimensions. Then drilling was performed to make holes for bolting. Fig. 1 shows the dimensions of the U-bend specimens used in this study.

Prepared specimens were stress relieved before bending at 150 °C for 1 hour. Then specimens were polished up to 1200 grit by silicon carbide emery papers to reduce scratches. U-bend specimens were bent by bolts made from the same material through ceramic insulators. U-bend specimens were cleaned by ultrasonic for 15 minutes, then decreased by acetone, rinsed with distilled water and dried by an air stream. The outer surface of U-bends was examined by Philips X230 scanning electron microscope to inspect whether any cracks have initiated after the SCC test duration.

In the present study, activated methyl diethanolamine (aMDEA) was the environment for SCC and cyclic polarization tests. Table 1 shows selected chemical and some physical properties.

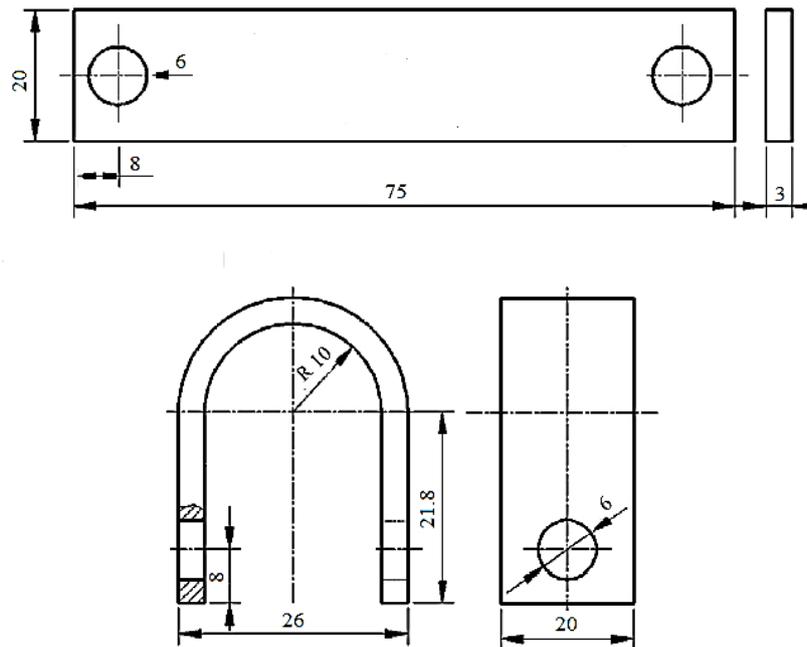


Fig. 1. Dimensions of U-bend specimens (millimeters).

Table 1. Chemical and physical properties of aMDEA solution used in this study.

Full chemical name	Activated Methyl Diethanol Amine
Chemical formula	$C_3H_{13}NO_2$
Molar mass (g/mol)	119.17
Boiling point ($^{\circ}C$)	247
Freezing point ($^{\circ}C$)	-21
Flash point ($^{\circ}C$)	127
Density at 20 $^{\circ}C$ (g/cm 3)	1.0426
Latent heat of vaporization (kJ/kg)	541.958

Fresh aMDEA was supplied as the base environment for corrosion and SCC initiation tests. To study how solution concentration affects SCC initiation of grade 430 stainless steel, aMDEA solution of 30, 40 and 50 wt% was used which were diluted by deionized water. Sealed containers were used for keeping solutions. SCC and corrosion tests were done at 25 and 70 $^{\circ}C$ within ± 2 $^{\circ}C$. In order to deaerate solutions, nitrogen gas (99.999%) was purged to solutions for 1 hour. Then 99.99% CO_2 gas was purged into all of the solutions until stability of pH, afterward U-bend specimens were immersed in prepared environments for the duration of 60 days. The schematic of the process is shown in one of our previous work [16].

Table 2 shows the test conditions used for the specimen coding in this study. Specimen nomenclature consisted of 2 couples of numbers as the temperature in degree Celsius and amine concentration based on weight percent.

After the SCC test duration, U-bend specimens were removed from amine solutions, washed with water and acetone. The apex of specimens was examined for possible initiated cracks by Scanning Electron Microscope (SEM), model Philips X230.

Table 2. Nomenclature of specimens and test conditions

Temperature ($^{\circ}C$)	aMDEA concentration (wt%)
25	40
70	50

Results and discussion

Materials characterization

Table 3 shows the chemical analysis of grade 430 stainless steel. Since this grade is ferritic, the amount of Ni is very low and Cr is the second major element, after Fe. Also, selected mechanical properties of supplied 430 stainless steel are provided in Table 4.

Table 3. Chemical analysis of supplied material, 430 stainless steel

C	Mn	Si	Cr	Ni	Mo	S	P	Fe
0.08	0.4	0.5	17.1	0.35	<0.05	<0.03	<0.006	Bal.

Table 4. Mechanical properties of supplied material, 430 stainless steel

UTS (Mpa)	YS (Mpa)	Elong. (%)	Hardness (BHN)
496±13	306±9	23±1.7	153.3±2.2

X-ray diffraction pattern of 430 stainless steel can be seen in Fig 2. As shown in the figure, ferrite (α) peaks are sharp and indicate planes of the BCC structure of the ferrite phase. These peaks are in conformity with the accepted patterns for this alloy [17].

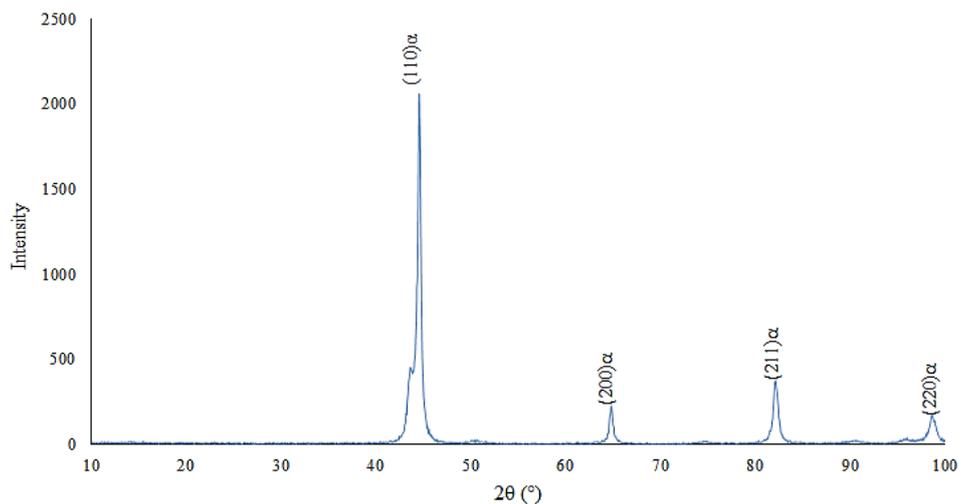


Fig 2. X-ray diffraction pattern of grade 430 stainless steel

Cyclic polarization

Figs. 3-5. shows corrosion behavior of grade 430 specimens in the 30, 40 and 50 wt% aMDEA solution. As understood from the figures, E_{corr} is the same at both 25 and 70 °C, while i_{corr} and especially i_p have increased from 25 to 70 °C. This result clarifies the role of temperature in anodic behavior even in a passive manner.

Also, the stability of the passive layer ($E_{\text{pp}}-E_b$) has decreased at the higher temperature. Temperature increment would increase reaction kinetics, degradation and oxidative agents which destabilize the passive layer at high potentials. At higher temperatures, cations at the interface of the metal-passive layer diffuse faster through passive layer toward electrolyte, which weakens passive layer stability, increases current density and enhances corrosion rate. Also, previous studies have shown that temperature increment acidifies amine solutions since it drops pka values [18]. Hydrogen diffusion rate (D_{H^+}) and activity (μ_{H^+}) are increased at higher temperatures, thus corrosion kinetics accelerates [19]. Degradation products which are resulted from high-temperature reactions, facilitate electron pass since they amplify electrical conduction of the amine solution [3,15].

The absence of beneficial elements like Ni and Mo in ferritic stainless steel grades lowers the efficiency of the passive layer. Previous studies have claimed that Mo decreases current density in the active region, shifts corrosion potential to more noble values and also increases the durability of the passive layer [20].

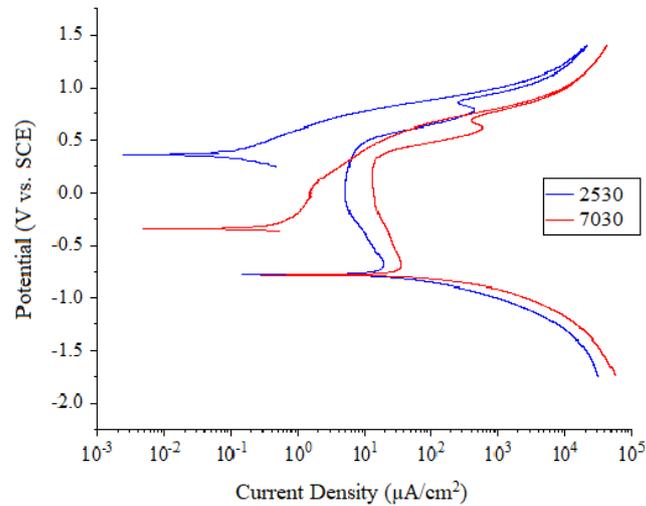


Fig 3. Cyclic polarization curves of grade 430 stainless steel in 30 wt% aMDEA at 25 and 70 °C.

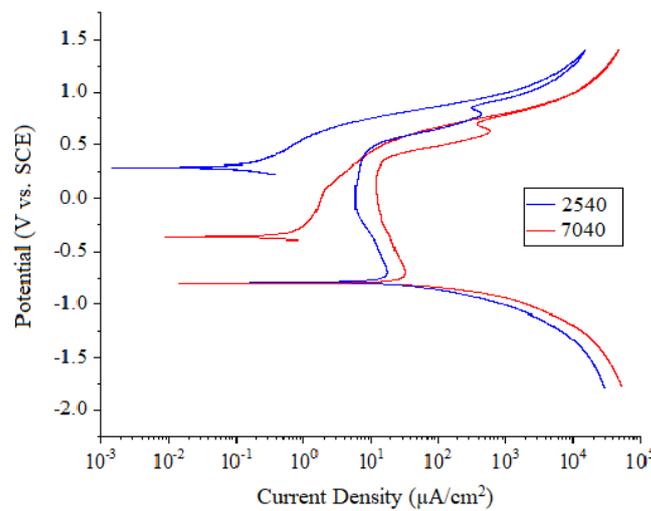


Fig 4. Cyclic polarization curves of grade 430 stainless steel in 40 wt% aMDEA at 25 and 70 °C.

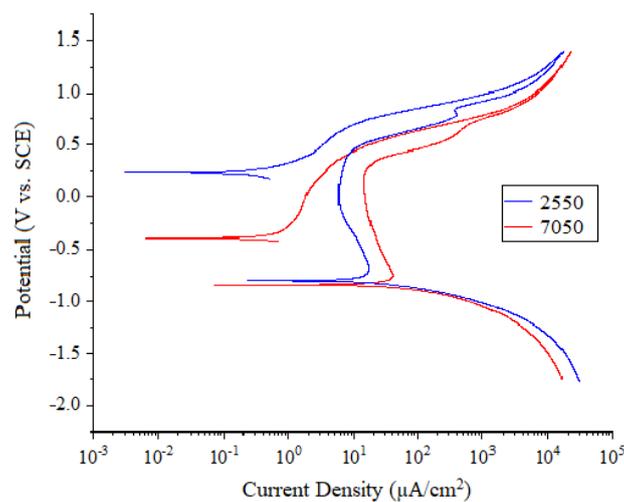


Fig 5. Cyclic polarization curves of grade 430 stainless steel in 50 wt% aMDEA at 25 and 70 °C.

By comparing results from Table 5, it is obvious that increasing amine solution concentration enhanced the corrosion rate.

Table 5. Numeric results of cyclic polarization tests of 430 stainless steel specimens in aMDEA solution.

Sample	E_{corr} (V)	i_{corr} ($\mu\text{A}/\text{cm}^2$)	E_{pp} (V)	i_p ($\mu\text{A}/\text{cm}^2$)	E_b (V)	$E_{pp}-E_b$ (V)	CR (mpy)
2530	-0.8	20.51	-0.72	5.12	0.49	1.21	14.13
7030	-0.79	35.45	-0.73	13.35	0.38	1.12	24.43
2540	-0.78	24.51	-0.71	5.73	0.48	1.19	16.89
7040	-0.78	39.47	-0.72	12.05	0.34	1.06	27.21
2550	-0.8	26.85	-0.71	5.8	0.44	1.15	18.50
7050	-0.83	46.36	-0.72	15.18	0.30	1.03	31.96

The more amine concentration, the more bi-carbamate and also more degradation products. Mentioned species increase corrosion kinetics [4,21]. Following reactions explain how corrosion rate increases in more concentrated amine solution [22]:



On the other hand, there are more H^+ ions in concentrated amines based on reaction 4. H^+ ions are the foundation of corrosion reactions and hydrogen-induced cracking (HIC). Fig. 6 summarizes the correlation of i_{corr} , amine concentration, and temperature.

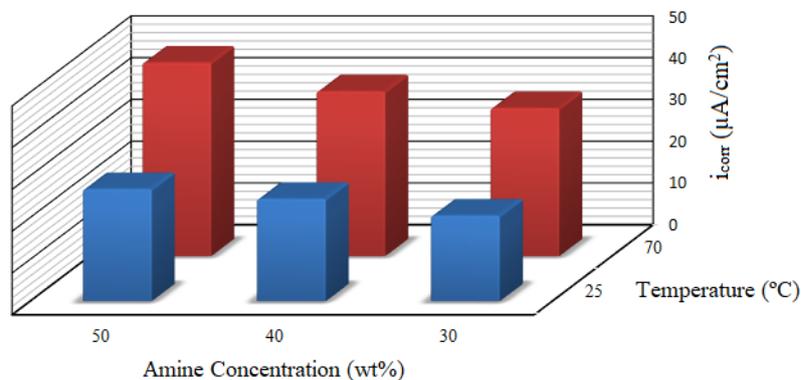


Fig. 6. Correlation of i_{corr} , amine concentration, and temperature.

Stress corrosion cracking

Fig 7. shows typical cracks which were identified on the surface of U-bend specimens. Micro-cracks were perpendicular to the loading axes as can be seen from the figure. The crack tip has a 45° direction that implies how maximum shear stress has facilitated the crack initiation [23].

Table 6 indicates the average size of cracks on the U-bend specimens. The size of the cracks has increased at higher temperatures and concentrated amine solutions. Each parameter that leads to a higher corrosion rate could intensify SCC since anodic dissolution has a significant role in film rupture mechanism²⁴. In this mechanism, the passive layer which is consisted of oxides is broken by stress. At this time, crack tip which provides fresh metal could react with the solution and will corrode. Also, a galvanic couple is formed between the passive layer and unprotected metal at the crack tip, due to the nobility of the passive layer.

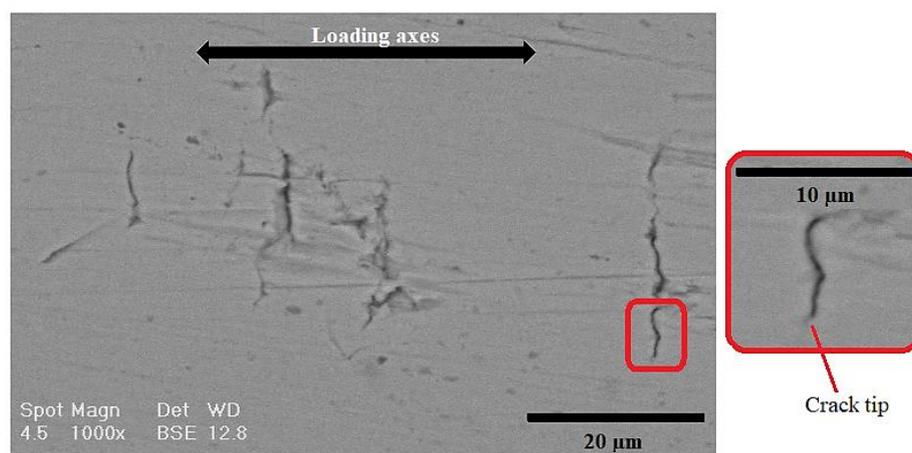


Fig. 7. Typical cracks on the surface of U-bend specimens

Table 6. Micro-crack length at 25 and 70 °C in different concentrations of aMDEA after the U-bend SCC test.

Sample	Micro-crack length (µm)
2530	12± 1.3
7030	12.4 ± 4.36
2540	13.63± 2.8
7040	17.84± 6.17
2550	21.21± 1.2
7050	32.4± 1.5

Conclusions

1. For the grade 430 stainless steel investigated in this study corrosion and cracking in aMDEA containing environment was observed. Therefore it could be concluded that in amine-containing environments this steel is not a very suitable alternative for carbon steels, which are commonly used in these environments.
2. The corrosion rate of grade 430 stainless steel increased in aMDEA solution with an increased in aMDEA concentration from 30 to 50 and also temperature from 25 to 70. This was due to the higher absorption rate of acid gases, bi-carbamate, H⁺ ion, degradation product and a higher rate of reactions.
3. The initiation of micro-cracks happened mainly 45° and 90° respect to the loading axis which is in accordance with the maximum shear stress.
4. Longer cracks were formed at high temperatures and amine concentrations. This was explained by the faster kinetics of corrosion reactions at the elevated temperatures and also amine concentrations.

Acknowledgments

The authors would like to appreciate the supports of Isfahan University of Technology.

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