# The Corrosion Characterization in Simulated Heat-Affected Zones of X80 Pipeline Steel in Near-Neutral Solution

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Received: 18 August 2015 / Accepted: 12 September 2015 / Published: 30 September 2015

The microstructure evolution and corrosion characterization under elastic stress in near-neutral chloride bearing solution of X80 pipeline steel simulated heat-affected zone (HAZ) were studied. It is shown that the corrosion resistance in fine grain HAZ (FGHAZ) is the best which can be attributed to the fine grains and the uniform distribution of M/A islands. In addition, the corrosion resistance of coarse grain HAZ (CGHAZ) with high peak temperature is the weakest which can be attributed to the coarse microstructure. In addition, relatively high heat input should be taken to improve the corrosion resistance in CGHAZ. It is found that four couples of galvanic effects exist at least which can promote the occurrence of localized corrosion. The presence of two obviously different parts in corrosion morphologies and the presence of pitting holes which locate in M/A islands sites on base material and CGHAZ surfaces can be attributed to the galvanic effects.

Keywords: heat-affected zone (HAZ); pitting; corrosion morphologies; galvanic effects

# **1. INTRODUCTION**

The high strength pipeline steel, such as X80 steel, has been used widely to transport the oil and natural gas due to its relatively high flow rates and low cost [1-3]. However, corrosion has been one dangerous threat affecting the safety and integrity of pipeline, especially in the presence of applied stress [4-6]. In generally, pipeline steels mainly experience two types of stress corrosion cracking (SCC), near-neutral-pH SCC and high-pH SCC respectively. The near-neutral SCC occuring in electrolyte with a pH about 6.5 has been studied for decades years [7] which occurs transgranularly and exhibited quasi-cleavage fracture [8,9]. In addition, previous studies have shown that its fracture

mechanism is mainly attributed to the combined effects of applied stress, hydrogen permeation and anodic dissolution [1,6,10-12]. It has been demonstrated that the applied stress or strain can enhance the hydrogen permeation and the anodic dissolution of steel in near-neutral solution, especially the plastic stress [6,13,14]. What's more, the cathodic current is disadvantage for SCC due to the hydrogen permeation [2,12,15].

It is found that heat-affected zone (HAZ) has weaker corrosion resistance than base metal and welded material with or without stressing levels in near-neutral solution or high-pH solution [16,17]. In addition, the appropriate heat treatment can improve the corrosion resistance in HAZ through changing the microstructure, but still worse than base material [17]. On the other hand, localized corrosion has been the most common failure mode for the high strength pipeline steels buried underground and the microstructure nonuniformity can promote it. Previous studies showed that pits and micro-cracks can be generated due to the presence of galvanic effects among different phases [4] even the presence of non-metallic inclusions [18,19]. However, the high strength pipeline steel is common dual-phase steel [20] to get high strength and toughness. More specifically, the complex microstructure gradients in HAZ are formed due to the presence of peak temperature gradients from welded material to base material. There may be galvanic effects between different zones, microstructures or phases and their preferentially dissolution are different. The phenomenon that pipeline steel SCC frequently occurred at welded joint observed in field can be attributed to this reason [10]. However, there is almost no further experiments evidence to support this theory.

In this study, the electrochemical corrosion behaviors and corrosion morphologies of base material and simulated HAZs in near-neutral solution with a relative high stress were studied to investigate the differences of different microstructures. It is anticipated to obtain some information and conclusions for this issue.

# 2. EXPERIMENTAL

### 2.1 Materials and solution

The composition of X80 pipeline steel used in this study is (wt.%): C 0.046, Si 0.305, Mn 1.76, P 0.007, S 0.001, Al 0.058, Nb 0.079, V 0.008, Ni 0.225, Cr 0.023, Mo 0.226, B 0.00025, Ti 0.015, Ca 0.001, Cu 0.215 and Fe balance. The test solution used in this study was NS4 solution which contains  $0.483 \text{g} \cdot \text{L}^{-1}$  NaHCO<sub>3</sub>,  $0.122 \text{g} \cdot \text{L}^{-1}$  KCl,  $0.181 \text{g} \cdot \text{L}^{-1}$  CaCl<sub>2</sub>·2H<sub>2</sub>O and  $0.131 \text{g} \cdot \text{L}^{-1}$  MgSO<sub>4</sub>·7H<sub>2</sub>O. Before the test, the solution was purged with the gas flow of 5% CO<sub>2</sub> balanced with N<sub>2</sub> for 1h to get a near-neutral condition (pH=6.8) and the gas flow was maintained in the whole tests. The temperature maintained 25°C during the whole tests.

## 2.2 The thermo-mechanical simulation processing

The HAZ samples used in this study were obtained through thermo-mechanical simulation processing by Gleeble 3500 machine. Several 10mm×1mm×150mm rectangular samples were cut

from X80 pipeline steels of 26.4mm thickness and then dried for 1h at 150°C. The vacuum levels were down to  $10^{-9}$  atm in the machine during heating and cooling cycles. The samples were heated up to different peak temperature at a rate of 160°C/s and then cooled down to ambient temperature. The specific parameters are shown in Fig.1 and Table 1.



Figure 1. The schematic diagram of the thermo-mechanical simulation processing

**Table 1.** The specific parameters of thermo-mechanical simulation processing

	FGHAZ	CGHAZ-1	CGHAZ-2	CGHAZ-3	CGHAZ-4
Heat input E (kJ/cm)	30	30	30	10	55
Peak temperature (°C)	950	1200	1350	1350	1350

## 2.3 The immersion and electrochemical measurements

The schematic diagram of specimens for the corrosion experiments is shown in Fig.2 in which it can be seen the area exposed to the solution is  $1 \text{cm}^2$  and the electrochemical measurements were performed on this rectangle-type area. Prior to the immersion and electrochemical measurements, the specimens were grounded up to 800 grit emery paper along the tensile direction, cleaned with acetone, alcohol and distilled water in sequence and then mounted in silica gel. In the immersion and electrochemical tests, the stress of 500MPa which is close to the yielding strength was applied on the specimen.

A three-electrode electrochemical cell system was employed with the use of the studied material as the working electrode, platinum plate as the counter electrode, and saturated calomel electrode (SCE) of +0.241  $V_{SHE}$  as the reference electrode. The potential used in this study is relative to SCE. The open circuit potential (OCP) measurements were carried out for 48h for every electrode. The electrochemical impedance spectroscopy (EIS) measurements were carried out with 10 mV amplitude and 0.01 Hz to 10 kHz frequencies after immersion a certain time. The potentiodynamic

polarization scans were carried out with a sweep rate of 0.5 mV/s. In addition, the potentiostatic polarization current measurement at -0.3V was conducted. To eliminate the experimental errors, every measurement was conducted for five times indicating that the data obtained was reliable.



Figure 2. The schematic diagram of specimens for the corrosion experiments

# 2.4 Microstructure and Corrosion morphologies observation

Microstructure observations of base material and HAZs were carried out by JSM—6480LA scanning electron microscope (SEM) after etching with 4% Nital (4 mL nitric acid and 96 mL ethanol) and EM-002B transmission electron microscopy (TEM) with 200kV accelerating voltage after mechanical thinning and twin-jet electro-polishing to about 10  $\mu$ m. The surface corrosion morphologies of every electrode after immersion for 48h were also conducted by SEM.

# **3. RESULTS**

#### 3.1 The microstructure analysis

## 3.1.1. The microstructure of base material

The microstructure of X80 pipeline steel base material used in this study is shown in Fig.3. It is shown that the X80 steel is one kind of dual-phase steel, The microstructure is polygonal ferrite with fine grain and granular bainite embellished by martensite plates and retained austenite (so called M/A islands) as the secondary phase. In Fig.3 (b), it can be seen clearly that the dislocation density in granular bainite zone is much higher than the polygonal ferrite zone. It has been demonstrated that the appropriate dual-phase design can promote the mechanical properties, especially the high-deformation capacity [20-22].



Figure 3. The morphologies of base material microstructure (a) SEM (b) bright field of TEM

#### 3.1.2 The microstructure of HAZs

It is known that the HAZ microstructure depends highly on the applied welding thermal cycles [16,23,24] in which the peak temperature and heat input are responsible for the process of nucleation and growth of the grains. It can be seen that an obvious microstructure gradient is generated due to the peak temperature differences in Fig.4 (a)-(c). It is shown that the FGHAZ microstructure is mainly polygonal ferrite with finer grains than base material which is beneficial to the mechanical properties as the Hall-Petch form. In addition, a little sum of M/A islands as secondary phase can be seen which distributes more dispersively compared with base material. However, the microstructure in CGHAZ-1 and CGHAZ-2 is mainly granular bainite in which the prior austenite grain boundaries and granular bainite grain boundaries are embellished by M/A islands. In addition, the M/A islands are parallel to each other in one prior austenite grain, but not in different austenite grains. What's more, the prior austenite grain size in CGHAZ-2 is much larger than CGHAZ-1 due to the higher peak temperature.

The prior austenite grain size is similar for the CGHAZs with the same peak temperature and different heat inputs, as is shown in Fig.4 (c)-(e). The microstructure in CGHAZ-3 is mainly bainite ferrite in which the M/A islands present needle-like with high length-width ratio. It is known that the lower the heat input, the higher the condensate degree and the more the nucleation sites resulting that the ferrite lath and M/A islands are much narrower. However, the microstructure is coarsened seriously when the heat input is 55 kJ/cm as is shown in Fig.4(e). The M/A islands show coarsen granular-like with low length-width ratio. In addition, the Widmannstatten ferrite can be seen near the prior austenite

grain boundaries. What's more, it can be seen clearly that the concentration of M/A islands decreases and the size increases as heat input increases for the CGHAZs with the same peak temperature.



**Figure 4.** The SEM micrographs of microstructure in HAZs (a) FGHAZ (b) CGHAZ-1 (c) CGHAZ-2 (d) CGHAZ-3 (e) CGHAZ-4

# 3.2 The electrochemical characteristics

It has been demonstrated that the corrosion characterizations in HAZ are complex due to the microstructure gradients [24-27] although there is almost no difference in the composition of HAZ. It is necessary to study the corrosion characterization differences of HAZ in NS4 solution with 5%  $CO_2$  under constant applied stress.

# 3.2.1 OCP

The OCP time dependence of different electrodes in the studied condition is shown in Fig.5. It is seen that the OCP values of all electrodes shifted negatively at first and tended to be stable after about several hours indicating that the electrochemical measurements should be conducted after immersion for several hours to make sure the results accuracy.

It can be seen that the OCP is obviously different for different electrodes indicating that the galvanic effect (the first couple of galvanic effect) will be introduced when the welded joint is immersed in the solution. It is known that the more negative the OCP, the higher the driving fore to be attacked. It is apparent that the OCP of base material is more negative than FGHAZ and much more positive than CGHAZ indicating that the CGHAZ may be attacked preferentially. In addition, the OCP of CGHAZ-1 is more positive than CGHAZ-2. In addition, it can be seen that there is a high content increase of OCP with the increasing of heat input.



Figure 5. The change regular of OCP vs. immersion time of different electrodes in the studied condition

#### 3.2.2 The EIS characterization

The EIS measurements were carried out to study the effects of microstructure on corrosion behaviors under different immersion time. The Nyquist diagrams under immersion for 1h, 2h, 4h, 8h, 24h, 48h, 72h and 96h were shown in Fig.6. It can be seen that the impedance feature of all electrodes under different immersion times is similar, i.e., only depressed semicircle in the first quadrant over the whole measured frequency range. The electrochemical equivalent circuit of  $R_s(Q_{dl}R_{cl})$  was used to fit the impedance data, in which  $R_s$  is solution resistance,  $Q_{dl}$  is the constant phase element (CPE) for the double-charge layer and  $R_{ct}$  is the charge transfer resistance. The CPE was used as the non-ideal capacitance (n<1) to account for heterogeneities of the double-charge layer, as:  $Z_{CPE} = [Q(jw)^n]^{-1}$ , where  $j = \sqrt{-1}$ , n is the CPE exponent, and w is the angular speed. Actually, pure capacitive behavior is represented by n=1 and Warburg resistance is represented by n=0.5. Fig.7 shows the fitted values of charge transfer resistance  $R_{ct}$  which can represent the corrosion resistance.

It is apparent that the change regulars of the size of the semicircle and  $R_{ct}$  are the same which depends highly on the microstructure and immersion time. It is seen that  $R_{ct}$  increases at initial 24h for all electrodes which can be attributed to the oxidation of the initially fresh surface and the formation of relatively thick corrosion product layers on the steel surface. For base material, CGHAZ-1, CGHAZ-2 and CGHAZ-3,  $R_{ct}$  continues to decrease as the immersion time increases continuously. However,  $R_{ct}$  increases continuously for FGHAZ and CGHAZ-4 although the increase extent slows down. It is indicated that there must be different phenomena happened on different electrodes surface indicating that it needs further studies.



**Figure 6.** The Nyquist plots of electrodes under different immersion time (a) base material (b) FGHAZ (c) CGHAZ-1 (d) CGHAZ-2 (e) CGHAZ-3 (f) CGHAZ-4



**Figure 7.** The fitted results of charge transfer resistance R<sub>ct</sub> of different electrodes under different immersion time

#### 3.2.3 The potentiodynamic polarization characterization

Fig.8 shows the results of potentialdynamic polarization measurements of different electrodes in the studied condition. It is apparent that all electrodes are in active state and the anodic processes are controlled by charge-transfer processes indicating that all electrodes are unable to be passivated in the measured corrosion condition and potential range. The plots were simulated by Tafel Curve Fitting methods to get the anodic and cathodic Tafel slopes ( $b_a$  and  $b_c$ ), corrosion potential ( $E_{corr}$ ) and corrosion current density ( $i_{corr}$ ). The fitting results are shown in Table 2. It is seen that the values series of the corrosion potential ( $E_{corr}$ ) are in accordance with OCP. However, it can be seen that the difference in anodic and cathodic Tafel slopes can be negligible indicating that the minor effect of microstructure evolution on the corrosion kinetics. In addition, it is shown that the corrosion current densities for different electrodes are in the same orders of magnitude and the differences among them can be ignored.



**Figure 8.** The potentiodynamic polarization curves of the base material and HAZs in the studied solution with the applied stress of 500MPa

	base material	FGHAZ	CGHAZ-1	CGHAZ-2	CGHAZ-3	CGHAZ-4`
$b_a(V/dec)$	0.161	0.147	0.157	0.166	0.171	0.181
b <sub>c</sub> (V/dec)	-0.549	-0.529	-0.589	-0.569	-0.552	-0.565
$E_{corr}$ (V .SCE)	-0.652	-0.625	-0.685	-0.770	-0.825	-0.708
$i_{corr}$ ( $\mu$ A/cm <sup>2</sup> )	10.66	9.68	18.20	13.44	25.84	19.27

**Table 2.** The corrosion potential  $(E_{corr})$  and corrosion current density  $(i_{corr})$  obtained from Fig.8 by Tafel Curve Fitting methods

It is indicated that no correlation between the microstructure evolution and the corrosion rate of different electrodes at corrosion potential can be seen when the electrodes were immersed into the solution individually which is in accordance with the previous study [24]. But there are obviously differences in the current densities in anodic polarization zones can be seen, the series are FGHAZ<br/>base material <CGHAZ-1<CGHAZ<4<CGHAZ<2<CGHAZ-3.

## 3.2.4 Anodic potentiostatic current density measurements

Fig.9 shows the time dependence of anodic dissolution current density of the base material and HAZs potentiostatically polarized at -0.3V (SCE). It is seen that the anodic dissolution current density series are in accordance of anodic zone of potentiodynamic polarization curves. It is shown that the anodic dissolution current density of FGHAZ is lower than base material and the anodic dissolution current density of CGHAZ is higher than base material. The anodic dissolution current density of CGHAZ-1 is lower than CGHAZ-2 indicating that the higher the peak temperature, the anodic dissolution current density. In addition, it is evident that the lower the heat input for those CGHAZs with the same peak temperature, the higher the anodic dissolution current density.



Figure 9. The anodic current density of different electrodes potentiostatically polarized at -0.3V (SCE)

# 3.3 Corrosion morphologies analysis

# 3.3.1 The effects of immersion time on the corrosion morphologies of base material

It can be seen clearly by naked eyes that the surface of the specimen after immersion in the studied solution can be divided into two obvious different parts. In one part, the surface of the specimen is bright and the corrosion products have fallen off the surface when the specimen was taken out from the solution so that it can be called "corrosion product desquamate" (CPD) zone. However, in the other part, the corrosion product is adhered to the dark and dim surface of the specimen strongly in which the corrosion products can not be divided by ultrasonic cleaning with alcohol so that it can be called "corrosion rates. The surface of the CPD zone is lower than the CPA zone indicating that the corrosion rate of the former is higher. It is indicated from Fig.10 that the proportion of the CPD increases linearly at first and then it will stabilize at about 50% after 2days.

The corrosion morphologies of base material in the CPD zone under different immersion time are shown in Fig.11. As is shown in Fig.10 (a), the surface of the sample becomes rough and asperous after immersion for 4h. The scratches left in the electrodes preparation processing can't be seen indicating that the corrosion depth is bigger than the depth of the scratches at least. However, the microstructure can not be identified clearly and no obvious pitting holes can be seen. In Fig.10 (b), it can be seen that the microstructure of polygonal ferrite and granular bainite has been clearly identified after immersion for 1 day. In addition, some small pitting holes can be seen in granular bainite zones. Fig.10 (c) shows that many big pitting holes can be seen clearly in the grain boundaries are prominent and the grain sags from the grain boundaries is better than the inner grain which can be attributed to the collection of alloying elements, such as Cu, in the grain boundaries. What's more, the similar corrosion morphologies can be seen after immersion for 4 days.



Figure 10. The effects of immersion time on the proportion of the CPD zone



Figure 11. The corrosion morphology of X80 in NS4 solution (a) 4h (b) 1 day (c) 2 days (d) 4days





**Figure 12.** The SEM micrograph and EDS result of corrosion product layer generated in the CPA zone (a) the SEM micrograph (b) The corresponding EDS result

The SEM micrographs of the corrosion product film that adhered in the CPA zone after immersion for 4 days in the NS4 solution are shown in Fig.12(a). It is indicated that the bright beam-shaped corrosion products didn't cover the whole surface and the scratches left in the sample preparation processing can be seen clearly in the exposed part indicating that the corrosion is not serious compared to the CPD zone. From the EDS of the CPA zone, it is indicated that the corrosion product is rich in Ca and Fe.

## 3.3.2 The corrosion morphologies in HAZ

The similar changes of area ratio of CPD zones can be seen in corrosion morphologies of HAZ surface during the immersion measurements which is not shown.



**Figure 13.** SEM of corrosion morphologies in CPA zone of HAZs after immersion for 2 days (a) FGHAZ (b) CGHAZ-1 (c) CGHAZ-2 (d) CGHAZ-3 (e) CGHAZ-4

The corrosion morphologies in CPD zones of HAZs after immersion for 2 days are shown in Fig.13. Fig.13 (a) shows that there is almost no pitting hole can be seen in FGHAZ surface in this magnification after immersion for 4 days.

Fig.13 (b) shows that the corrosion morphologies of CGHAZ-1 present river-like shape and some pitting holes can be seen. However, it seems difficult to identify where the pitting holes locate. Fig.13 (c) shows that many big pitting holes can be produced along the prior-austenite grain boundaries or inner of the prior austenite on CGHAZ-2 surface. In addition, some close pitting holes grow up to connect with each other resulting that some cracks are generated. In Fig.13 (d), it is shown that many dense and favaginous pitting holes can be seen and many holes have grown up to connect with others on CGHAZ-3 surface. The density of pitting holes is much higher than CGHAZ-2 although the size is smaller. Furthermore, it is interesting that the pitting holes line is parallel to the M/A islands and bainite lath in one austenite grain. However, the pitting corrosion of CGHAZ-4 is not seriously which is shown in Fig.13 (e). It is shown that there is only a little sum of pitting holes which locate on coarse M/A islands.

## 4. DISCUSSION

# 4.1 The corrosion mechanism

During the corrosion process of the steel in NS4 solution with 5%CO<sub>2</sub> under the applied elastic stress, the anodic reaction established is the oxidation of iron [13,28,29]

 $Fe \rightarrow Fe^{2+} + 2e$  (1)

The dissolution of  $CO_2$  and the ionization of  $H_2CO_3$  reactions would happen when the gas flow was purged [29,30]:

 $CO_{2} + H_{2}O \rightarrow H_{2}CO_{3} (2)$   $H_{2}CO_{3} \rightarrow HCO_{3}^{-} + H^{+} (3)$   $HCO_{3}^{-} \rightarrow H^{+} + CO_{3}^{2-} (4)$ 

The cathodic reaction is the reduction of  $H^+$  [23] or the formation of the OH<sup>-</sup>[6,8,13,28]:

 $\mathrm{H}^{+} + \mathrm{e} \rightarrow \mathrm{H}_{\mathrm{ads}} (5)$ 

 $\mathrm{H_{2}O} + \mathrm{e} \rightarrow \mathrm{OH^{-}} + \mathrm{H_{ads}} \ (\mathrm{6})$ 

In addition, the reactions 7 and 8 can also happen in cathode. However, it has been demonstrated that they are thermodynamically less favorable than the reactions 5 and 6 due to the negative standard electrode potential [23]. It means that reactions 5 or 6 are the main cathodic reactions.

 $\begin{array}{l} H_2CO_3 + e \rightarrow H_{ads} + HCO_3^- (7) \\ HCO_3^- + e \rightarrow H_{ads} + CO_3^{2-} (8) \end{array}$ 

The  $H_{ads}$  means those hydrogen atoms which are adsorbed onto the steel surface. The  $H_{ads}$  atoms may combine to hydrogen molecule on the steel surface or become absorbed into the steel as the concentration of  $H_{ads}$  increases continuously. They can expressed as follows:

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    H_{ads} + H_{ads} \rightarrow H_2  (9)
    H_{ads} \rightarrow H_{abs}  (10)
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It has been demonstrated that the presence of applied stress would enhance the reaction 10 which can cause the hydrogen embrittlement phenomenon [1].

During the corrosion process, the carbonate corrosion product can form and deposit on the steel surface, as follows [7,9,.13,29,30]:

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Fe^{2+} + HCO_{3}^{-} \rightarrow FeCO_{3} + H^{+} (11)
Fe + 2H_{2}O \rightarrow Fe(OH)_{2} + 2H^{+} + 2e (12)
Fe(OH)_{2} + HCO_{3}^{-} \rightarrow FeCO_{3} + H_{2}O + OH^{-} (13)
Fe^{2+} + CO_{3}^{2-} \rightarrow FeCO_{3} (14)
Ca^{2+} + CO_{3}^{2-} \rightarrow CaCO_{3} (15)
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what's more, some intermediate species, such as Fe(OH)<sub>ads</sub> can also be formed on the electrode surface [10,29]:

 $Fe^{2+} + H_2O \rightarrow Fe(OH)_{ads} + H^+ + e (16)$  $Fe(OH)_{ads} \rightarrow Fe^{2+} + OH^- + e (17)$ 

### 4.2 The effects of microstructure on corrosion resistance

The results of electrochemical measurements and corrosion morphologies show that the corrosion characterization of different electrodes depends highly on the microstructure. The galvanic effect between different zones can be introduced due to the different open circuit potentials. It can be seen that the CGHAZ close to the base material would acts as anode and be attacked preferentially when the welded joint is immersed into the solution. More importantly, large cathode/ small anode phenomenon can be generated due to the CGHAZ is relatively narrow resulting that the dissolution rate in CGHAZ is promoted.

It is shown that the carbonate corrosion products film can be formed on steel surface in NS4 solution during the corrosion process whose stability is not satisfying. The fresh steel surface will be exposed to the solution as the corrosion products film is damaged which is responsible for the generation of obviously different two parts of CPD zone and CPA zone. In addition, the galvanic effect (the second couple of galvanic effect) can be introduced between the CPD zone and CPA zone which can promote the further corrosion of the CPA zone. In addition, the corrosion products film in the junction between two zones is easy to be attacked by Cl<sup>-</sup> due to the bigger contact area with electrolyte which is responsible for the continuously increase of CPD zone area during the initial immersion process. It is indicated that there are two contradictory processes. The continuously formation and precipitation of corrosion products are advantage for the corrosion resistance. However, the fallen off of corrosion products and the increase of CPD zone area are disadvantage for the corrosion resistance. During the initial immersion of 24h, the former predominates although the CPD zone area increases which is responsible for the increase of R<sub>ct</sub>. However, the latter is one reason, but not only, for the R<sub>ct</sub> changes regular immersion for 24h-96h because of the differences for different electrodes.

It has been demonstrated that the corrosion or dissolution priorities for different phases or microstructures in corrosion environments are different [31]. For example, the dissolution vulnerability of ferrite is higher than Fe<sub>3</sub>C in alkaline electrolyte [31]. It is shown in Fig.2 and Fig.3 that M/A

islands are presence in base material, FGHAZ and CGHAZ microstructure as secondary phase. The martensite is rich in carbon which is a kind of non-equivalent microstructure. It is expected that there must be micro-galvanic effect (the third couple of galvanic effect) between martensite and matrix. The martensite may be attacked preferentially and then a pitting hole is formed which can be responsible for the pitting holes locate in the M/A islands sites. What's more, another galvanic effect (the fourth couple of galvanic effect) could be introduced between the pitting holes and other zones. It can be expected that holes serve as anode due to the absence of ions in the holes which promotes the further dissolution of the holes regions.

However, the preferentially extent of the dissolution of martensite depends highly on the carbon concentration, the lattice distortion of martensite and the differences between martensite and matrix. It is known that the microstructure is fine in FGHAZ and the size of M/A islands is small which may result that the dissolution priority slows down. In addition the microstructure is coarsened seriously in CGHAZ-4. The widmannstatten and coarsen polygonal ferrite also have high dissolution priorities resulting that the dissolution priority of martensite slows down.

## 4.3 Implication for SCC

Previously studies have shown that near-neutral SCC depends highly on the interaction of hydrogen, stress and anodic dissolution [28]. It is shown that many pitting holes can be produced due to the preferentially dissolution of martensite presence in M/A islands and it is expected that the pitting holes zone can be a trap for hydrogen and stress centralization. In addition, the hydrogen and stress can promote the anodic dissolution of the pitting holes to make this zone weaker and weaker. What's more, some cracks may be formed as the pitting holes grow up, as is shown in Fig.12 which can result in the fracture of pipe. It is indicated that it is necessary to eliminate the formation and growth of pitting holes. In view of enhancing the corrosion resistance CGHAZ, the higher heat input should be taken to decrease the number pitting holes. For base material, it is necessary to make the grains more fine and the distribution of M/A islands more uniformity/ dispersively in view of the fine corrosion resistance and little pitting holes in FGHAZ.

# **4. CONCLUSIONS**

(1) The microstructure of FGHAZ is mainly polygonal ferrite with fine grain and the microstructure of CGHAZ from bainite ferrite to granular bainite as the heat input increases.

(2) There are four couples of galvanic effects at least, i.e. between base material and HAZ, between the CPD zone and CPA zone, between martensite and neighbors, between the pitting holes and other zones.

(3) The corrosion resistance depends highly on the microstructure and immersion time. The corrosion resistance of FGHAZ is the best and CGHAZ is the weakest. In addition, relatively high heat input should be taken to improve the corrosion resistance in CGHAZ.

(4) Many pitting holes can be seen in base material and CGHAZ corrosion morphologies after immersion for 2 days due to the preferentially dissolution of martensite of M/A islands.

(5) There is almost no pitting holes can be seen in FGHAZ which can be attributed to the fine grain and the uniform distribution of M/A islands. In view of this, the microstructure of base material should be optimized.

# ACKNOWLEDGEMENTS

The authors are grateful for the support of the National Natural Science Foundation of China (No.51271099).

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