Study on corrosion mechanism of the weld seam of submarine pipeline's spool

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Abstract. This paper studies the corrosion mechanism of the weld seam of the submarine pipeline's spool. The types and causes of inner tube weld corrosion are simulated by EDX and XRD analysis of the on-site pipe corrosion products, combined with OLGA Software simulation pipeline flow pattern. The tensile testing, impact testing and hardness testing were carried out on the base metal and the weld by tensile tester, pendulum impact tester and Brinell hardness tester to analyze the mechanical properties of the base metal and the weld; the microstructural difference between the weld and the base metal were analyzed by optical microscopy; The results show that the liquid phase flow rate along the line is between 3.5m/s and 7.5m/s, which aggravates the mixing between the gas and liquid phases to form a bubble flow. When the entire weld area is immersed in the same simulated medium solution, the galvanic corrosion occurs in three parts of the weld zone. The weld seam and heat affected zone will be accelerated to corrode as the anode region of the galvanic couple. The weld seam has the lowest corrosion potential and is always used as an anode to accelerate corrosion.

1 Introduction

The submarine pipeline is the lifeblood of offshore oil and gas gathering and transportation [1]. As the most important means of offshore oil and gas transportation, it has the advantages of being more efficient, energy-saving and safer than other modes of transportation. However, the operation cost of submarine pipelines is high and the operation is difficult. If a pipeline accident occurs, oil and gas leaks and even an explosion accident occurs. Corrosion not only affects the service life of submarine pipelines, but also affects their safety and reliability. Pipeline steel will undergo a series of unbalanced thermal cycling processes during welding, resulting in uneven distribution of microstructure of pipeline steel welds, inclusions, hardened microstructure, poor mechanical properties and the result of galvanic corrosion in the weld zone results in a decrease in the corrosion resistance of the weld. The medium currently transported by the submarine pipeline is multiphase flow mixed. The medium contains CO₂, Cl⁻ and water and many corrosive media, which will cause serious corrosion to the pipeline and weld [2]. During the pipeline transportation process,

temperature, pressure, stress and other factors will interact to accelerate the corrosion of the inner wall of the pipeline, resulting in faster corrosion rate [3]. The corrosion failure of oil and gas pipelines caused by internal corrosion is far more than the number of accidents caused by external corrosion [4].

The emergence of welding technology has greatly promoted the development of long-distance pipelines. However, during the welding process, the pipeline steel base metal and the weld zone need to undergo a series of complicated non-equilibrium thermal cycles, resulting in uneven microstructure of the weld and possibly welding defects. In general, the corrosion resistance of welded joints is poor, especially the position of the pipe ring welds often fails [5-6]. As a result of the thermal cycle of the weld, the microstructure of the welded joint changes significantly, and the composition and structure of the region become uneven, and the corrosion behavior is greatly affected. Corrosion of welded joints mainly includes local corrosion [7-8], stress corrosion [9-10] and galvanic corrosion [11-12].

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2 Pipeline situation

The pipe section studied in this paper is located between the flange of 2322.385m and the flange of 2357.015m. The linear distance is about 35m and there are 11 welds. The corrosion in the pipe section is serious, and the corrosion of the spool is serious and the total number of the corrosion defects is 336. The weld seams near the flange joint of the spool is severely corroded with 103 defects and the defect depth is up to 87%. The corrosion defect is shown in Figure 1.

Fig. 1. Weld corrosion defects

3 Simulation and Experiment

In the laboratory, scanning electron microscopy, energy spectrum analysis, X-ray diffraction and other experimental methods were used to conduct on-site sample collection. The sample information is shown in Table 1.

Table 1 The Sample information collected on site

No.	Clock orientation	Remarks	No.	Clock orientation	Remarks
1	6:00	-	3	6:00	Weld seam
2	0:00	-	4	0:00	30° Elbow

3.1 OLGA software simulates Pipe flow pattern

The multi-phase flow calculation model of the submarine pipeline was established by using OLGA software. The main calculation data is shown in Table 2.

Table 2. The Basic data of OLGA calculation

Project	Value	Project	Value
Spool Length (m)	38	Inner Pipe Diameter (mm)	254
Water Content	57.5	Inlet Pressure (kPa)	1800
Inner Pipe Wall Thickness (mm)	12.7	Outlet Pressure (kPa)	600
Inner Pipe	X60	Pipe Length (Km)	2.5
Outer Pipe Diameter (mm)	355.6	Inlet Temperature/K	319.5
Outer Pipe Wall Thickness (mm)	11.1	Total Heat Transfer Number (W/m ² K)	2.0

Outer Pipe	X52	Liquid (m ³ /d)	8657.6
Corrosion Allowance (mm)	1.27	Insulation Thickness (mm)	25
Gas (10 ⁶ Sm ³ /d)	0.128	Buried Depth (m)	1.5

3.2 Mechanical performance test

The test material is API-X60 pipeline steel with the chemical composition showed in Table 3. Before experimenting, the morphology of X60 steel is observed by optical microscope.

Table 3. Chemical composition (wt.%) of X60 steel

Element	C	Si	Mn	P	S	Nb	Ti	Al	V	N	Fe
Content (%)	0.12	0.025	1.05	0.002	0.006	0.003	0.013	0.025	0.008	0.007	bal.

The tensile test, also known as the tensile test, is a test method for measuring the tensile properties of materials under axial load. The experimental equipment is the MTS-810 tensile test machine. Impact testing is an experiment that evaluates the ability of a material to withstand a single impact load. The experimental equipment is the ZBC2302-D pendulum impact testing machine. The hardness of a material is the ability of a material to resist deformation, plastic deformation or damage.

3.3 Electrochemical test

Electrochemical tests are conducted by Gamry Reference 3000 in a three-electrode cell system. X60 steel mounted in epoxy resin with an exposure area of 1.0 cm² is used as the working electrode. It is fixed firmly in the cell, leaving only the upper surface exposed. Carbon rods act as counter electrode. A saturated calomel electrode (SCE) is used as the reference electrode. The simulating solution is prepared according to the analysis data of Offshore platforms. The main chemical compositions are given in Table 4.

Table 4. Simulated Solution

Cationic (mg/L)			Anion (mg/L)			
Na ⁺	Mg ²⁺	Ca ²⁺	Cl ⁻	HCO ₃ ⁻	CO ₃ ²⁻	S ²⁻
22208	114	260	21200	489	<2.0	<0.005

Polarization curves are measured potentiodynamically from -2.0 V (vs. SCE) to 1.25 V (vs. SCE) at a scan rate of 1 mV/s. EIS spectra for X60 steel during 96 h exposure in the electrolyte layers are acquired at open-circuit potential over the frequency range of 10⁵ ~ 10⁻² Hz. The equivalent circuits are fitted using the Zsimpwin software. All tests are performed at 50 ± 2 °C. All tests are repeated by three duplicate specimens to confirm reproducibility of the results, and the average of the three measurements is

reported in this work.

The galvanic corrosion test is mainly used to monitor the variation of galvanic current with time. The galvanic corrosion test is the same as the electrochemical test.

4 Results and discussion

4.1 On-site corrosion product analysis

According to scanning electron microscopy and XRD experiments, the composition and content of different parts of the corrosion products on site were obtained. The result is shown in Table 5.

Table 5 EDS and XRD experiments result

No.	SEM	EDS	XRD
1
2
3
4

It can see from Table 5, EDS results show that the main elements in the corrosion products are Fe, O and C. According to the XRD analysis, the corrosion product is Ferrous carbonate. There is a CO₂ corrosion environment in the pipeline. The whole process of corrosion reaction can be expressed by equations (1) – (8).

4.2 OLGA software simulation results

It can be seen from Figure 2 that the simulation results of pressure and temperature established by the model are

consistent with the actual ones.

Fig. 2. Pressure distribution

Fig. 3. HOL distribution

Fig. 4. Flow pattern distribution

As shown in Figure 3, the liquid holding rate along the pipeline is between 0.32 and 0.64, indicating that the flow condition in the pipeline is a typical gas-liquid two-phase flow. As shown in Figure 4, the whole pipeline exists in the form of slug flow. The slug flow liquid phase entrains a certain amount of air bubbles. At the end of the pipeline, the flow direction changes and the turbulent flow area easily leads to the appearance and accumulation of bubbles.

Fig. 5 Velocity distribution along the line

The HOL is the smallest near the end of the pipe (Figure 3), and the gas phase dominates. However, the lower pressure near the end point maximizes the gas-liquid phase flow rate (Figure 5), which exacerbates the mixing between the gas and liquid phases to form a bubble flow.

4.3 Optical microscope results

Inclusions and metallographic structure of the sample were observed by a metallographic microscope.

(a) Weld inclusions (b) Base metal inclusions

Fig. 6. Metallographic diagram

(a) Weld (b) Base metal

Fig. 7. Microstructure diagram

The parent metal has a uniform crystal distribution and a small size, mostly equiaxed crystals but no obvious coarse grains, which ensures good joint performance of the base layer. However, the microstructure of the weld specimen has different grain sizes and disorderly arrangement with poor corrosion resistance.

4.4 Mechanical performance

4.4.1 Tensile properties

Three sets of parallel tests were conducted on the base metal and weld samples respectively. The results of the tensile test were shown in Table 6. The samples before and after the tensile test were shown in Figure 8.

Fig. 8. Tensile test stress-strain curve

Table 6 The results of tensile test

No.	Yield Strength(MPa)			Average MPa	Tensile strength(MPa)			Average MPa	Elongation (%)		
Weld	4	4	4	46.3	5	5	5	54.5	13.	11.	12.
	4	6	7		4	4	5		37	85	49
	8	9	2		0	3	2				
Base metal	5	5	5	52.3	6	6	6	62.0	18.	18.	18.
	3	2	1		3	1	0		95	38	24
	1	2	6		9	6	5				

4.4.2 Impact properties

The impact test results under normal temperature conditions are shown in Table 7. It can be seen from Table 7 that the average impact energy of the weld impact specimen at normal temperature is less than the average impact energy of the base specimen impact specimen.

Table 7 Welding joint impact test data

No.	Impact energy /J			Average /J
Weld	163.66	162.41	161.02	162.36
Base metal	282.32	292.99	285.83	287.05

4.4.3 Brinell hardness

According to the experimental results, the Brinell hardness value is converted into Vickers hardness value, as shown in Table 8.

Table 8 Hardness test and regional average (HV)

No	Vickers hardness /HV			Average /HV
Weld	180	186	178	181.3
Base metal	187	194	189	190

4.5 Electrochemical

4.5.1 Corrosion properties

At a temperature of 50 °C, the polarization curves of the samples at various parts of the pipe are shown in Figure 9. The results of the polarization curve fitting are shown in Table 9.

Fig. 9. Polarization curve

Table 9 Electrochemical parameter

Sample	E_{corr} (Volts)	b_a (mV)	b_c (mV)	I_{corr} ($\mu\text{A}/\text{cm}^2$)
Weld	-0.6911	69.97	217.25	32.594
Heat affected	-0.6916	75.43	259.58	23.417
Base metal	-0.7157	67.77	167.78	18.232

It can be seen from Figure 9 and Table 9 that the corrosion current density ($32.594 \mu\text{A}/\text{cm}^2$) in the weld zone is significantly larger than the corrosion current density of the base metal ($18.232 \mu\text{A}/\text{cm}^2$). In the same corrosion environment, the local corrosion rate in the weld zone is higher than that in the base metal, which is consistent with the distribution of weld corrosion defects in the site.

The electrochemical impedance spectroscopy of each sample is shown in Figure 10. The equivalent circuit and the electrochemical parameters of each component based on the impedance spectrum are shown in Figure 11 and Table 10.

Fig. 10. Electrochemical impedance spectra of corrosion

Fig. 11 Equivalent circuit diagram

Table 10 Electrochemical parameters

Sample	$R_s/\Omega \cdot \text{cm}^{-2}$	$Q-Y/\Omega^{-1} \cdot \text{cm}^{-2} \cdot \text{s}^n$	$Q-n$	$R_t/\Omega \cdot \text{cm}^{-2}$
Weld	4.12	0.0020547	0.8045	247.9
Heat affected	3.96	0.0015269	0.7842	289.5
Base metal	3.759	0.002075	0.7822	566.2

4.5.2 Galvanic corrosion test results

The relation curve between the electric dielectric current and time in the simulated medium solution is shown in Figure 12.

Fig. 12. Current-time curve

The experimental results obtained in Section 4.4.1 indicate that the corrosion potential of the weld is the lowest. Due to the strong penetrability of Cl^- in the solution, the conductivity is strong, and the ions are continuously transported to cause the anode to react:

On the surface of the cathode, the cathode reduction reaction of the depolarizing agent is mainly carried out, and the rate of anodic dissolution reaction is small, almost negligible. According to the principle of electrochemistry, the relationship should be satisfied at this time:

$$\ln v = \frac{E_{k2} - E_{k1}}{\beta_{a1} + \beta_{c2}} + \frac{\beta_{c2}}{\beta_{a1} + \beta_{c2}} \ln \frac{I_{k2}}{I_{k1}} + \frac{\beta_{c2}}{\beta_{a1} + \beta_{c2}} \ln \frac{A_2}{A_1} \quad (12)$$

Where v -anode corrosion rate (mm/a); E_{k1} , E_{k2} - anode and cathode corrosion potential (V); I_{k1} , I_{k2} - corrosion current density ($\mu\text{A}/\text{cm}^2$); β_{a1} , β_{c2} — anode and cathode Tafel constants.

When $E_{k1} < E_{k2}$, they form a corrosive galvanic cell when they are in contact with each other. In the pipeline, the area of the base metal is much larger than that of the weld and the heat-affected zone, so the anode area ratio is small, and the corrosion current per unit area is high.

5 Conclusion

This paper analyzes the composition of corrosion products, the mechanical properties and corrosion properties of pipe materials in the field, and obtains the corrosion mechanism and rule of the welding seam of

submarine pipeline's spool. The main conclusions are as follows:

(1) The XRD and EDX test results of the corrosion product samples showed that the main elements in the corrosion product were Fe, O and C, and the main components of the corrosion product were FeCO_3 and Fe_3O_4 . The liquid phase velocity along the pipeline was 3.5 m/s-7.5 m/s, and the gas phase velocity near the terminal was up to 10 m/s, which may cause pitting corrosion.

(2) The results of metallographic experiments show that the matrix of the base metal sample has less inclusions and smaller size, and the weld sample has more inclusions and larger size. The tensile test results show that the tensile properties of the base metal tensile specimens are better, the tensile strength and yield strength of the weld specimens are lower, and the tensile fracture resistance is poor. The impact energy test results of the samples show that they all meet the specification requirements of more than 50J. However, the average impact work of the weld impact sample is significantly lower than that of the base material, so its resistance to deformation and fracture is lower than that of the base material. The hardness test results show that the hardness of the base metal and the weld are lower than the engineering requirements of less than 260 HV, the weld hardness is greater than the base metal hardness, poor corrosion resistance;

(3) The severity of corrosion in the inner tube of the spool is sequentially ranked as weld > heat affected zone > base metal. The corrosion rate of the weld is significantly larger than that of the base metal, and local pitting and galvanic corrosion occur at the weld. The weld-base metal galvanic current gradually increases to 8.83 μA over time, and the weld is used as the anode. Weld-heat affected zone galvanic couple, weld as anode, galvanic current gradually tends to 2.935 μA . Heat affected zone - base metal galvanic couple, heat affected zone as anode, galvanic current gradually tends to 0.95 μA . When corroded in the same environment, the base metal is protected as a cathode region, while the weld and heat affected regions act as an anode to accelerate corrosion.

To sum up, the comprehensive mechanical properties and corrosion resistance of the weld are lower than the base metal.

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