Hydrogen Embrittlement of Dissimilar Steel Welding Joints

Gao Xinxin, Liu Baocheng, Liang Xiaoming and Yu Lihua
Qingdao University of Science and Technology, weifang, Shandong  261500 , China
* Corresponding author: a Liu Baocheng, 369038133@qq.com

Abstract: Aiming at the problem of hydrogen embrittlement in dissimilar steel welded joints, the hydrogen permeation behavior and stress corrosion sensitivity of the material in sea water were studied by hydrogen permeation test, electrochemical test and slow strain rate tensile test (SSRT), and the fracture morphology was observed with SEM. The results show that the corrosion resistance and hydrogen permeation characteristics of dissimilar steel welded joints are obviously different. The corrosion resistance of the weld zone is between two parent materials. The corrosion resistance of A side HAZ is the worst, and hydrogen evolution reaction is easy. Under the condition of different polarization potential, the material gradually changes from ductile fracture to brittleness with the negative shift of the polarization potential. When the cathodic polarization potential is negative to -950 mV, the welding joints have obvious characteristics of hydrogen embrittlement.

1. Introduction
The welding of dissimilar metals can not only make full use of the excellent properties of the constituent materials, but also greatly reduce the production cost and significantly improve the economic benefits, so it is widely used in petrochemical, shipbuilding, aerospace and other fields[1]. it is inevitable that the high strength of its material will cause brittle fracture risk in the hydrogen evolution environment, making the failure of hydrogen related welded joints become more and more serious[2-4]. At present, a lot of researches have been done on the microstructure and mechanical properties of dissimilar steel welded joints, but few studies have been done on the hydrogen evolution properties of dissimilar steel welded joints [5]. Therefore, it is of great significance to study the hydrogen embrittlement behavior and the failure of dissimilar steel welded joints during service. This passage is about hydrogen permeation test of heterogenous high strength steel in sea water. Under the condition of hydrogen loading, the slow strain rate (SSRT) experiment and SEM fracture surface analysis are carried out. Combined with electrochemical test, the hydrogen embrittlement sensitivity of dissimilar steel welded joints is studied.

2. Experimental Materials and Methods
The experimental material is a butt welded joint of 0.8 strength ratio high strength steel. The size of the sample is 35 mm × 310 mm×320 mm, using the single side slope of the V shape and remaining 3 mm blunt edge. CO2 gas shielded welding (V840) was adopted for sample welding parts. The methods for obtaining part of the sample are as follows. After cutting the sample warp, it is eroded with 5% alcohol nitrate solution, which can clearly distinguish the area of the welded joint. Then the HAZ (near the fusion line) and the weld seam are cut off respectively, and the hydrogen permeation test and electrochemical test are carried out.
The 2273 electrochemical workstation are used in the electrochemical test. The sample is grind to 1500# by sand paper step by step, and the control area is 1 cm². The reference electrode and the auxiliary electrode are respectively saturated with calomel electrode (SCE) and platinum niobium wire. Select -600 ~200 mV (vs. Ecorr) as scanning potential interval. The scanning rate should be 20 mV/min.

The working area of hydrogen permeation test sample is 1 cm², and the thickness is 0.5 mm. The sand paper is polished to the mirror step by step. The experimental device is Devnathan-Stachurski and the mother cell is double electrolyzer[6]. Besides, the mother cell is the cathode for filling the sample and the sub electrolysis cell is the anode for detecting hydrogen permeation. The electroless nickel plating on the anode side samples is carried out before the experiment. Then 0.2 mol/L NaOH solution is added to the anode chamber to passivate the sample at constant potential (150 mV, vs Hg/HgO). The Hg/Hg0 electrode is a reference electrode, and the platinum niobium wire is a auxiliary electrode. It is not until the background current density is less than 10⁻⁷A/cm² that the seawater is added into the cathode chamber and the -1100 mV (vs SCE) potential is applied to cathodic polarization. The permeable hydrogen atoms can be oxidized rapidly to produce electric current. The saturated calomel electrode is used as the reference electrode, and platinum niobium wire is used as auxiliary electrode. The hydrogen permeation current generated by electrochemical workstation is monitored and recorded. The variation curve of hydrogen permeation current with time can be measured.

In slow strain tensile test (SSRT), specification of bar like tensile specimen meets the standard of GB/T 228-2010. The weld is in the middle position of the sample working section. The size of the working section is 5 ×50 mm, and the surface finish is R0.8. GYF-30 slow strain rate tensile test machine is used in the test and the tensile rate is 0.005 mm/min. The tensile test is carried out in the air and the natural sea water respectively. The interval of polarization potential is -800~-1000 mV, the reference electrode is saturated calomel electrode (SCE), and the auxiliary electrode is tinplate. After the experiment, the extension rate and the contraction rate of the fracture are measured with the vernier caliper, and the microstructure of the fracture is observed by scanning electron microscope (FEI/Philips XL30).

3. Results and Analysis

3.1 Electrochemical behavior

Dynamic potential polarization curve of different microregions of welded joint of dissimilar steel is shown in Figure 1 (A represents 800 MPa grade steel, and B represents 1000 MPa grade steel, the same below). The self corrosion potential and hydrogen evolution potential of the sample are obtained by fitting the polarization curve, as shown in Table 1. It can be seen that the corrosion potential from large to small, the hydrogen evolution potential ascending order: base metal B, weld, base metal A, HAZ of B, HAZ of A. Therefore, the corrosion resistance of the base metal B is better than that of the base metal A, and the tendency of hydrogen evolution is obvious. The corrosion resistance of the two sides of the HAZ is the worst, and the hydrogen evolution reaction is most likely to occur. Because the self corrosion potential of the welded joint is different, and the welded joint will form a galvanic galvanic cell. It can be seen that the electrode potential in the HAZ is the most negative, and will suffer accelerated corrosion in the multi electrode system. This may be related to the microstructure of the microregions of the welded joint of the dissimilar steel, especially in the large structure of the HAZ, the inclusions in the lattice and the cavitation defects, so the corrosion resistance is the worst [7].
Figure 1: Dynamic potential polarization curves of various micro regions in the welded joint of dissimilar steel

Table 1: The self-corrosion potential and hydrogen evolution potential of the sample

| Region     | $E_{corr}$ (mV) | Hydrogen evolution potential (mV) |
|------------|-----------------|----------------------------------|
| B-base     | -467            | -890                             |
| WM         | -496            | -894                             |
| A-base     | -564            | -881                             |
| B-HAZ      | -546            | -870                             |
| A-HAZ      | -588            | -859                             |

3.2 Hydrogen permeation behavior

The hydrogen permeation current density curves of different regions of welded joints of heterogeneous high-strength steel are shown in Figure 2. The hydrogen permeation of metal can be measured by the current density of the saturated anode $i_\infty^{[8]}$. It can be seen from the diagram that the hydrogen permeation current density increases rapidly and then reaches the stable state with the increase of time. The current density of saturated hydrogen permeation is the smallest of base metal B. The weld zone is $2.19 \times 10^{-6}$ A/cm$^2$, and the saturated hydrogen permeation current density of the base metal A is slightly larger than that of the base metal B. The hydrogen permeation current density in the HAZ is the smallest. The greater the density of the hydrogen permeation current, the more easy the hydrogen atom in this material is to pass through. That is, the greater the tendency of hydrogen evolution in materials is. It can be seen that the A side HAZ of the welded joint of the dissimilar steel is in a dangerous area for hydrogen evolution.

Figure 2: Hydrogen permeation current density curves of various micro zones of dissimilar steel welding joint
Table 2 The hydrogen diffusion flux $J_\infty$, effective diffusivity $D$ and Solubility hydrogen $C$ in different regions of welding joint

|       | $J_\infty$ (mol/($m^2\cdot s$)) | $D_{eff}$ ($m^2/s$) | $C$_{mol/m$^3$} |
|-------|---------------------------------|--------------------|-----------------|
| A-HAZ | $4.24\times10^{-7}$            | $1.16\times10^{-11}$ | 9.15            |
| B-HAZ | $3.18\times10^{-7}$            | $1.07\times10^{-11}$ | 7.43            |
| A-Base| $2.52\times10^{-7}$            | $9.18\times10^{-12}$ | 6.85            |
| WM    | $2.27\times10^{-7}$            | $1.30\times10^{-12}$ | 4.36            |
| B-Base| $1.43\times10^{-7}$            | $9.17\times10^{-13}$ | 3.89            |

According to the formula of hydrogen permeation experiment\cite{9-10}, the results of hydrogen permeation experiment in different regions of the welded joint of dissimilar steel are shown in Table 2. The effective diffusion coefficient of hydrogen in each micro zone of the welded joint is between $9.17 \times 10^{-13}$~1.16 ×10$^{-11}$ m$^2$/s. The diffusion coefficient of hydrogen in both sides of the heat affected zone is the largest and has a relatively strong hydrogen diffusion capacity. The welding joints of the solubility of hydrogen from large to small is as follows, HAZ of A , HAZ of B, base metal A, the weld zone, and the base metal B. The solubility of hydrogen can be used to characterize the efficiency of hydrogen entering into metal under a given hydrogen charge condition. The greater the diffusion hydrogen concentration, the higher the efficiency of hydrogen into the material.

3.3 Hydrogen Embrittlement

Figure 3 is the stress and strain curves of dissimilar steel welded joints under different tensile conditions. It is known that the stress strain curve almost coincides with the elastic stage, and there is no obvious upper and lower yield point. However, the strain of dissimilar steel welded joints gradually decreases with the negative shift of the polarization potential.

Table 3 is the mechanical parameters of dissimilar steel welded joints. The elongation and contraction rate of the sample in the air reach its maximum. They are 15.20%, and 65.19% respectively. At this point, the plasticity of the specimen is the best, while the value in the sea water decreases and the plasticity also decreases. With the negative polarization potential, the elongation and section shrinkage of the welded joint decreases significantly. The sensitivity of hydrogen embrittlement increases gradually. When the polarization potential is -1100 mV, the shrinkage and elongation of the specimen are 12.29% and 30.56% respectively. And the minimum value is reached. In the process of dynamic stretching, the entry of hydrogen atoms leads to a reduction in the bonding force between the atoms of the matrix. As the applied potential becomes more negative, the amount of hydrogen atom aggregates much more and the bond force also decreases much more.

Figure 3. The stress-strain curves of dissimilar steel welding joints at different cathodic polarization potential
Figure 4 is about hydrogen embrittlement coefficient of different polarization potential, which is obtained by section shrinkage and elongation. Hydrogen embrittlement sensitivity is commonly used in engineering to evaluate the sensitivity of hydrogen embrittlement\cite{12}. $F_H = (\psi_0 - \psi) / \psi_0 \times 100\%$. In formula, $F_H$ represents hydrogen embrittlement coefficient, $\psi_0$ represents test samples in the air, and $\psi$ represents the cross-section shrinkage of the specimen in the corrosive medium. It is obtained from the diagram that the hydrogen embrittlement coefficient of the welded joint of the dissimilar steel increases with the negative shift of the polarization potential. In the potential interval of $E_{corr} \sim -900$ mV, the hydrogen embrittlement coefficient fluctuates within 25%, the loss of mechanical properties is small, and the material is in the safety zone. When the polarization potential is greater than -950 mV, the hydrogen embrittlement coefficient is greater than 25%, and the material enters the danger zone. When the polarization potential is about -940 mV, the hydrogen embrittlement coefficient is 25%. At this time, the welded joint is at the best protective potential\cite{10}.

Table 3 Mechanical parameters of dissimilar steel welded joints

| $E$/mV | $\delta$/% | $\psi$/% | $F_H$/% |
|--------|-----------|--------|--------|
| Air    | 15.02     | 65.19  | 0      |
| $E_{corr}$ | 14.86     | 60.73  | 5.55   |
| -800   | 16.7      | 61.97  | 9.84   |
| -850   | 15.98     | 54.21  | 16.84  |
| -900   | 14.62     | 51.00  | 21.77  |
| -950   | 13.72     | 47.19  | 27.61  |
| -1000  | 13.09     | 45.24  | 30.60  |
| -1100  | 12.29     | 30.56  | 53.12  |

Figure 4. Hydrogen embrittlement coefficient of dissimilar steel welding joints at different polarization potential

3.4 Fracture morphology analysis

The fracture micromorphology of the welded joint of the dissimilar steel under different conditions is shown in Figure 5. After stretching in the air (Figure 5 (a, b)) and in sea water (Figure 5 (c,d)), there is a clear necking in the fracture (b) is the equiaxed dimple shape, and the plastic toughness is good. The dimples in the sea are smaller and lighter than the dimples in the air. There have no brittle phenomenon, and toughness has declined. When the polarization potential is at -800 mV, the necking is reduced and the dimple is further reduced and shallower, and a few tear cracks appear (Figure 5 (e,f)). When the polarization potential is at -900 mV, the fracture still has plastic deformation but is lower than that of -800 mV. Dimple area reduces, crack area increases, and the river pattern and solution theory appear (Figure 5 (g, h)). As the polarization potential reaches -950 mV, the fracture is not obvious. The rift area increases, and the river pattern and solution theory appear, which is characterized by obvious quasi cleavage and typical brittle fracture (Figure 5 (i, j)).
Fig. 5 Micro fracture morphology of dissimilar steel welded joints at different tensile conditions
(a,b) Air, (c,d) \( E_{\text{corr}} \), (e,f) -800 mV, (g,h) -900 mV, (i,j) -950 mV

To sum up, with the negative shift of the polarization potential, the hydrogen content in the welded joint of the dissimilar steel increases and the plastic loss of the material increases. The fracture mode gradually changed from toughness to brittleness. When the potential is negative to -950 mV, there are obvious characteristics of hydrogen embrittlement, which is the same as -940 mV which is the best cathodic protection potential obtained by the hydrogen embrittlement coefficient.

4. Conclusions

(1) According to the polarization curve, the corrosion resistance of the weld zone is located between the base metal A and the base metal B, both of which are larger than the HAZ on both sides. The corrosion resistance of the A side HAZ is the worst, and the hydrogen evolution reaction is easy to occur.

(2) The solubility of hydrogen in dissimilar steel welded joints ranges from large to small in order of A side HAZ, B side HAZ, base metal A, weld, base metal B. It can be seen that the tendency of hydrogen absorption in the A side HAZ is the most, which is a dangerous area for welding joint to cause hydrogen corrosion and hydrogen damage more easily.

(3) With the negative shift of the polarization potential, the hydrogen content in the dissimilar steel welded joint increases, and the plastic loss increases. The fracture mode gradually changes from ductile to brittle direction. When the potential is negative to -950 mV, the obvious characteristics of hydrogen embrittlement appear. To sum up, the optimum cathodic protection potential of the material is -940 mV.

Reference

[1] Huang Bensheng, Huang Longpeng ,Li Hui. Research Status and Development Trend of Dissimilar Metals Welding[J]. Mater Rev, 2011, 25(23): 118-121.

[2] Hardie D, Charles E A, Lopez A H. Hydrogen Embrittlement of High Strength Pipeline Steels[J]. Corros Sci, 2006, 48(12): 4378-4385.

[3] Lindley C, Rudd W J. Influence of the Level of Cathodic Protection on the Corrosion Fatigue Properties of High Strength Welded Joints[J]. Marine Structures, 2001, 14(4): 397-416.

[4] Batt C, Ddodson J, Robinson M J. Hydrogen Embrittlement of Cathodically Protected High Strength Steel in Sea Water and Seabed Sediment[J]. British Corrosion Journal, 2002, 37(3): 194-198.
[5] Zhang Shuting, Zhou Youlong, Li Xiongbing, et al. Analysis on Microstructure and Mechanical Properties of the welded joints on 900 MPa and Q345B dissimilar steels [J]. Electric Welding Machine, 2015, 45(09): 107-109.

[6] Li H, Wang Z, Chen L, et al. ChemInform Abstract: Research on Advanced Materials for Li-Ion Batteries [J]. Advanced Materials, 2009, 21(45): 4593-4607.

[7] Zheng Chuanbo, Tang Zhujun, Shen Xiaolan. Effect of microstructure on hydrogen embrittlement of 2205 duplex stainless steel [J]. Heat Treatment of Metals. 2015, 40(09): 39-44.

[8] Liu Yu, Li Yan, Li Qiang. Effect of cathodic polarization on hydrogen embrittlement susceptibility of x80 pipeline steel in simulated deep sea environment [J]. Acta Metallurgica Sinica, 2013, 49(9): 1089-1097.

[9] LIU Q, ATRENS A D, SHI Z, et al. Determination of the hydrogen fugacity during electrolytic charging of steel [J]. Corrosion Science, 2014, 87(5): 239-258.

[10] Tan Wenzhi, Du Yuanlong, Fu Chao. Environmental embrittlement of zc-120 steel in sea water induced by cathodic protection [J]. Materials Protection, 1998, 21(3): 10-13.