Effect of static hydrogen charging on corrosion and hydrogen embrittlement of High strength steel

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Abstract: The corrosion and hydrogen embrittlement properties of 1000MPa grade high strength steel in sea water are studied by weightlessness test under the condition of cathode polarization and slow strain tensile test (SSRT) after static hydrogen filling. The fracture characteristics of the specimen are observed with SEM. The results show that the most positive cathodic protection potential of high strength steel in sea water is -780 mV. The tensile test shows that with the negative shift of the polarization potential and the increase of hydrogen charging time, the elongation and the shrinkage of the high strength steel decrease gradually. The fracture mode transforms from ductile to cleavage and intergranular fracture. It can be seen that the toughness of the material decreases and the hydrogen embrittlement sensitivity increases gradually. Especially, the effect of polarization potential on hydrogen embrittlement of materials is more obvious.

1. Introduction
In recent years, the application of high-strength steel in navigation has been increasingly widespread. However, due to the harsh marine corrosion environment, we must consider the safety and reliability of high-strength steel, and do well in corrosion protection[1,2]. Cathodic protection technology is widely used for corrosion protection of high strength steel at home and abroad[3-5]. In cathodic protection, if the protective potential is too high, the corrosion of steel will not be well suppressed. Excessive potential will lead to over protection of high-strength steel[6]. Moreover, as the strength level of steel increases, hydrogen embrittlement sensitivity will increase significantly[7]. At present, there are few studies on the performance of 1000 MPa grade high strength steel in marine corrosive environment at home and abroad. Therefore, it is of great practical significance to study the effect of static hydrogen charging on corrosion and hydrogen embrittlement of 1000 MPa grade high strength steel.

2. Experimental Materials and Methods
The basic material used in the test is the 1000 MPa grade high strength steel plate with a thickness of 20 mm. The main chemical composition is shown in Table 1.

The specimen size in zero-G test is 100×30×2mm as shown in Figure 1. The samples are ground by sand paper, washed and dried by alcohol, and weighing is recorded. One end of the sample is welded with a wire, and the epoxy filler is used to seal the connection part. The Vernier caliper is used to precisely measure the bare size of the sample and calculate the area. The cathode is polarized by electrochemical workstation. Five potentials (-750mV, -800mV, -850mV, -900mV, -950mV) are selected for cathodic protection. The polarization time is 15 days, and three parallel specimens are selected at different potentials. The experimental results are averaged. After the test period is finished,
the corrosion products are removed and pickled (acid washing liquid: 1.1g/cm³ hydrochloric acid 1000mL and six times methyl four amine 20g). After drying and weighing, the corrosion rate and protection degree can be calculated by comparing the sample parameters under the self-corrosion condition. After corrosion, the macroscopic morphology is observed by HIROX 3D video microscope (KH-3000V).

Table 1 Chemical composition of the base metals (mass fraction, %)

| Material content | C   | Si  | Cr  | Mn  | Ni  | P   | Cu  | Mo  | Fe  |
|------------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|
|                  | 1.1 | 7.1 | 8.2 | 6.3 | 10.2| 0.09| 10.2| 4   | 52.81|

Figure 1 shape and size of weightless specimen

Slow strain rate tensile test (SSRT) uses rod like specimens, and the specification conforms to GB/T228-2010 standard. The working section size is Φ 5× 50mm. The other parts are sealed with 704 silica gel and the surface finish is R0.8. First, the sample is charged with hydrogen under the constant potential. The cathodic potential applied is -800 mV, -900 mV and -1000 mV respectively. The hydrogen filling time is divided into 7 days, 14 days and 21 days. Three parallel samples are selected at different potentials, and the experimental results are averaged. After the polarization is charged, the sample will be removed. Besides, the hydrogen content of some specimens is measured immediately, the other is washed by the brush and is dried with the cold wind, so as to prevent the hydrogen atom exudation from the metal to be stretched on the stretcher immediately. The electronic universal testing machine (CMT5205/5305) is used at a tensile rate of 0.005 mm/min. The reference electrode is a saturated calomel electrode, and the auxiliary electrode is lead plate. The polarization potentials are -800mV, -900mV and -1000mV (vs SCE) respectively. The stress-strain curves of the specimens are recorded during the tensile test until the specimens are fractured. At the end of the experiment, the elongation at break and the contraction rate of the section are measured immediately. Macro morphology of the fracture are observed by XL-30 scanning electron microscope.

3. Results and analysis

3.1 Corrosion resistance
The corrosion of 1000MPa grade high strength steel under different cathodic charging potentials is studied by Zero-G test. According to the technical specification for anticorrosion of steel structures in JTS153-3-2007 Harbor Engineering, the cathodic protection of the underwater area should be more than 90%. Therefore, using (self-corrosion rate\ corrosion rate under protection) to symbolize the most positive protective potential namely protection degree that reaches 90%\[^8\].

Figure 2 The curve of polarization current density and time for high-strength steel at different potential
The current density-time curve of 1000MPa grade high strength steel under different polarization potentials is shown in Figure 2. It can be seen that the current density curve increases slowly at first and then increases smoothly. And gradually it increases with the negative displacement of the applied potential. When the polarization potential is -750mV, the current density is about 3.63µA·cm\(^{-2}\) and is at a minimum value. When the potential is -950mV, the current density is the largest and reach at 11.32 A·cm\(^{-2}\).

The formula for calculating the corrosion rate and degree of protection of the specimen is shown below. (C and C\(_0\), the corrosion rate of materials under constant potential and self-corrosion. unit mm/a; m\(_1\) and m\(_3\), the weight of the material before and after the test, unit g; \(\rho\), material density, unit g/cm\(^3\); t, time, unit d; A, the working area of the sample, unit cm\(^2\))

\[
C = \frac{(m_3 - m_2) \times 365 \times 10}{\rho \times t \times A}
\]

\[
P = \frac{C_0 - C}{C_0} \times 100\%
\]

The formula for calculating the corrosion rate and degree of protection of the specimen is shown below. The corrosion rate and protection degree of 1000 MPa high strength steel under different polarization potentials are calculated from the above formula as shown in Table 2. It can be seen that the corrosion rate and protection degree of high strength steel decrease gradually and increase with the negative shift of polarization potential. Under the condition of corrosion, the corrosion rate of high strength steel is 0.0202mm/a, when the potential is -750mV, the corrosion rate is 0.0202mm/a, the protection degree is 80.87%, and the corrosion tendency is weakened. When the potential is shifted to -850mV, the corrosion rate is only 0.0095mm/a, and the protection degree reaches 91.03%. With the negative shift of protective potential being -900mV and -950mV, the corrosion rate has been very small, and the protection degree has reached over 95%. At this point, 1000MPa grade high strength steel has been well protected.

Table 2 The corrosion rate and degree of protection of high-strength steel under different potential

| polarization current density /(µA·cm\(^{-2}\)) | The corrosion rate /(mm/a) | degree of protection /(%) |
|-----------------------------------------------|---------------------------|---------------------------|
| \(E_{corr}\) / | 0.1056 | 0 |
| -750 mV | 3.36 | 0.0202 | 80.87 |
| -800 mV | 6.98 | 0.0095 | 91.03 |
| -850 mV | 8.08 | 0.0059 | 94.45 |
| -900 mV | 8.97 | 0.0053 | 95.01 |
| -950 mV | 11.32 | 0.0046 | 95.63 |

Figure. 3 is the curve of corrosion rate and degree of protection with polarization potential of high strength steel. The Gauss fitting of the curve shows that when the polarization potential is -780 mV, the protection degree of high strength steel is 90%. Therefore, according to the JTS153-3-2007 standard, it can be concluded that the most positive cathodic protection potential of 1000MPa high strength steel in seawater environment is -780 mV.
3.2 Hydrogen embrittlement sensitivity of high strength steel

Figure 4 is the stress-strain curve of high strength steel. It can be seen from the diagram that under the same polarization hydrogen charging time, the strain of 1000 MPa grade steel decreases gradually as the polarization potential shifts. It decrease from about 11.8% to 9.61%, the reduction is around 2%. At the same cathodic polarization potential, with the increasing of hydrogen charging time, the strain decreases. When the cathodic polarization potential is -800 mV, the strain will decrease from 11.8% to 11.5%. When the polarization potential is -1000 mV, the strain will decrease from 9.61% to 9.34%. At the same cathodic polarization potential, the strain range of materials with different static hydrogen charging time is small, and it is about 0.3%. The above results show that the influence of cathodic polarization potential on the strain rate of high-strength steel is more significant than that of hydrogen charging time.

Figure 4 The stress-strain curves of 1000 MPa-grade high strength steel at different hydrogen charging conditions

The change curves of post failure elongation and section shrinkage of 100 MPa grade high strength steel with static hydrogen charging time are shown in Figure 5. Under the same cathodic polarization potential, the elongation at break and section shrinkage of 1000 MPa grade high strength steel decrease with the increase of static hydrogen charging time. But the volatility is small. The range of the elongation of the sample with static hydrogen charging is less than 1% and the fluctuation range of the shrinkage is less than 5%. Under different static hydrogen charging time, the elongation range of the specimen is less than 0.6%, and the contraction range of the section is less than 5%. However, at different cathodic polarization potentials, Going with the negative shift of polarization potential, the elongation at break and section shrinkage of 1000 MPa grade high strength steel decrease greatly. The fluctuation range of elongation is less than 3%, and the fluctuation range of sectional shrinkage is less than 25%. In summary, the increasing of hydrogen charging time can reduce the ductility and brittleness of metals, but the influence on the mechanical properties of materials is weaker than that of cathodic polarization. Because of the negative polarization potential, dislocation can carry a large number of hydrogen atoms in metal in a short time, resulting in hydrogen embrittlement[9].
The relationship between the hydrogen content at break and the time of static hydrogen charging can be obtained by gas analyzer (Figure 6). It can be found that the hydrogen content of samples is different under different polarization potentials. But all of them increase with the time of static hydrogen charging. Under the same static hydrogen charging time, the fluctuation of hydrogen content under different polarization potentials is about \( (1.7) \times 10^{-6} \text{ L/g} \). Under the same cathodic polarization potential, the hydrogen content of the fracture of high strength steel increases gradually with the increase of static hydrogen charging time. But the range of numerical fluctuation is small and it is about \( (0.2-2.9) \times 10^{-6} \text{ L/g} \). It can be seen that in a certain range, with the negative shift of cathodic polarization potential, the more hydrogen is added into the high-strength steel, the larger the increase is. However, the hydrogen content of high strength steel fracture at the same polarization potential increased slightly with the increase of static hydrogen charging time, The static hydrogen charging time has little effect on the material\(^{[10, 11]}\).

The fracture morphology of 100 MPa grade high strength steel is shown in Figure 7. It can be seen that when the potential is -800 mV, there are some dimples on the surface of the fracture surface, which shows the characteristics of ductile fracture. With the increase of the static hydrogen filling time, the proportion of the dimple tissue in the fiber zone of the fracture gradually decreases. The shape is slightly smaller and shallower, and a small area of river pattern appears on the surface. When the hydrogen filling time was 21 days, the surface area of the fracture surface increased and there was a little tear, and the material began to have brittle fracture characteristics. At -900 mV potential, the fracture toughened fossa is less and not obvious, there are a large number of river patterns, and with the increase of hydrogen filling time, the formation of a large number of ripping edges and discontinuous, fracture tendency is obvious. It is characterized by quasi cleavage fracture. It can be seen that the fracture begins to change to brittle fracture. Under the potential of -1000 mV, the necking of fracture breaks away, and there are a lot of cracks on the surface. With the increasing of hydrogen charging time, the grain has a significant three-dimensional sense. After 14 days of static hydrogen charging, the fracture of the intergranular dimple appears on the surface of the sample, showing the characteristics of intergranular fracture, and the material was in the dangerous brittle fracture area.
With the negative shift of the cathodic polarization potential, the hydrogen loss in the welded joint increases, and the plastic loss increases, and ductile fracture gradually transforms into brittle fracture. When the potential is negative to -900 mV, there is obvious hydrogen embrittlement. Moreover, the hydrogen embrittlement sensitivity of different static hydrogen charging time is weaker than that of cathodic polarization potential. The tensile test in the seawater environment after static hydrogen filling shows that with the negative shift of the polarization potential and the increase of hydrogen filling time, the elongation at the end of the 1000 MPa grade high strength steel and the shrinkage rate of the section gradually decrease. The fracture mode is transformed from ductile to cleavage and intergranular fracture. The toughness of the material gradually decreases and the hydrogen embrittlement sensitivity gradually increases. Especially, the effect of polarization potential on hydrogen embrittlement of materials is more obvious.

Figure. 7 Micro fracture morphology of high strength steel at different polarization potential and different static hydrogen charging time

4. Conclusions
(1) The most positive cathodic protection potential of 1000MPa grade high strength steel in seawater is -780mV. When the polarization potential is negative to -800mV, there is almost no corrosion phenomenon on the surface of the metal.
(2) The tensile test in the sea water environment after static hydrogen filling shows that with the negative shift of the polarization potential and the increasing of hydrogen filling time, the elongation at the end of the 1000 MPa grade high strength steel and the shrinkage rate of the section gradually decrease. The fracture mode is changed from ductile to cleavage and intergranular fracture. The toughness of the material decreases and the hydrogen embrittlement sensitivity increases. Especially, the effect of polarization potential on hydrogen embrittlement of materials is more obvious.

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