CORROSION RESISTANCE INVESTIGATION OF TITANIUM AND STAINLESS STEEL IN SATURATED H_2S SEA WATER

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Abstract: In the waters near the sewage outlets of the land and special waters such as the Black Sea, it contains quantities of corrosive substances such as SO_4^{2-}, S^{2-}, HS^- , which is a great challenge for the application of submarine products. For those titanium alloys products, the dense oxidation film layer is naturally able to protect the whole structure from corroding. However, under the high density of hydrogen circumstance, hydrogen absorption reaction on titanium is the most likely risk which could result in hydrogen embrittlement and stress corrosion cracking failure. In this paper, analysis shows that it will cost far more than 25 years for hydrogen embrittlement failure on titanium; and the RPTs, deployed by laid and/or sand buried which are subject to very small tensile stress during the service period, do not meet the necessary conditions of corrosion stress cracking failure. The corrosion tests in simulated seawater with saturated H_2S show no corrosion phenomenon which is observed on titanium alloy samples and the corrosion rate is < 0.0001mg/a; stainless steel samples coated with special films are observed with slight corrosion bulging. The size of corrosion bubbles is less than 10 μm and the corrosion rate of this coated stainless steel material is among 0.0001～0.0005 mm/a, which is recognized as corrosion resistance material.

1. INTRODUCTION

As is known to all, titanium alloys are widely used in aerospace, military, biomedical, petrochemical, seawater desalination and other high-tech fields due to high titanium element reserves in the crust. With the development of science and technology and the recognition and excavation of titanium alloy, people began to try and explore the application of titanium alloy in the new field, such as corrosion resistance. China has the largest total reserves of titanium in the world, which provides infinite possibilities and space for the application and development of titanium alloys. In recent years, many research institutes and enterprises in China have actively invested in the modification of titanium alloy materials and have continued to extend the application field of titanium alloy materials. In the field of marine corrosion resistance, titanium alloy corrosion resistant materials have been used for years in the Atlantic Ocean, the Indian Ocean, the Pacific Ocean, and the Arctic Ocean. And also, been successfully applied to the Black Sea area with high H_2S content.

As a marine corrosion resistant material, titanium alloy is mainly used to manufacture seawater desalination equipment, ships and worship, oil platform equipment and so on. Titanium alloy materials can withstand seawater because of the two most useful features: corrosion resistance and the highest strength -weight ratio in metals. The study shows Titanium metal can almost be mixed with any metal in the molten state to form various alloys, which has given the excellent and unique properties of titanium alloy. TIMET[1] studies and discusses the hydrogen embrittlement corrosion and corrosion resistance mechanism of titanium alloy materials. The results show titanium and its alloy have excellent anti-seawater corrosion resistance and hydrogen brittleness performance in seawater.

As reported in many papers[2,3], the fatal weakness of titanium alloy are hydrogen absorption and hydrogen embrittlement fracture. In open air, the hydrogen embrittlement of titanium alloy is affected by hydrogen and tensile stress, and brittle fracture occurs under external force after hydrogen absorption to saturation.

Although titanium has a strong hydrogen absorption capability, titanium is obviously passivated when the hydrogen gas contains 2% water. Even if the pressure reaches 5.5MPa, the temperature reaches 316°C, and hydrogen absorption does not occur. At the same time, the oxide passivated film produced on the titanium surface helps to stop the hydrogen permeation, even in the environment without oxygen, the passivation film on the titanium surface can be recovered quickly after damage.
Therefore, in seawater, the penetration of hydrogen in titanium alloys is not as fast as expected, According to the Fick diffusion law(1):

$$J_A = -D_{AB}\frac{dC_A}{dZ} \qquad (1)$$

Where, J_A-diffusion time, D_{AB}-diffusion coefficient.
If the hydrogen partial pressure and the ambient temperature are constant in the diffusion process, the diffusion volume and diffusion coefficient can be regarded as linear relationship. The time required for the [H] to enter the entire titanium housing can be calculated based on the following formula(2). The theoretical calculation value is far more than the 25-year service life of the RPT and BU at the bottom of the sea.

$$t = \frac{S}{D} = 3.26\times 10^{16} Years \qquad (2)$$

For the failure mechanism of stress corrosion cracking, it is generally believed that hydrogen is slowly diffused to a place with high stress field intensity to form hydride, and micro-cracks are generated in the matrix -hydride interface or substrate, and then micro-cracks are extended and fractured under stress. The process must be in stress and the hydrogenation of titanium alloy reaches the required hydrogen content. According to the material handbook[2], the formula for calculating the concentrated stress at the crack tip when the titanium alloy material is broken is shown as follows:

$$\sigma_c = \frac{K_{1c}}{\sqrt{\pi \sec\frac{\pi a}{W}}\cdot\sqrt{\pi a}} \qquad (3)$$

Where, σ_c-Concentrated stress on crack tip during fracture; K_{1C}-Stress intensity factor during fracture; W-Crack width; a-Crack length.

According to the formula, For RPT, the stress fracture tension induced by hydrogen is about 30KN, which is far less than the measured broken value. In addition, the RPT is deployed on the seabed where the RPT does not bear the tensile stress, the tensile stress is equal to or close to 0KN at this situation.

According to the descriptions above, the probability that titanium absorbs hydrogen in seawater until facture is very low. However, in some high-corrosion areas, such as in the Black Sea of High Hydrogen Concentration, we need to focus on the corrosion effect of H_2S on titanium alloy materials. As described in the study[4,5], the density of H_2S in Black Sea is 1.5-2.25ml/L, which is equivalent to the maximum 3.4 ppm. The H_2S concentration in the 1500m water depth of the Black Sea is about 8-10ml/L, equivalent to 12.1-15.1μg/g.

TIMET[1] describes the performances of titanium and titanium alloys in various corrosive environments. As shown in Table 1, titanium is completely corrosion-resistant to dry H_2S gas, wet H_2S gas and H_2S aqueous solution. Under the test conditions of the NACE (NATIONAL ASSOCIATION OF CORROSION ENGINEERS): The oxygen-free solution dissolves 3000ppm H_2S, 5%NaCl, 0.5% acetic acid, and PH of the solution keep 3.5, After 30 days of immersion, the tested titanium samples have no hydrogen reaction and stress cracking.

Under the recommended test conditions of ASTM G38-73, the titanium samples are subjected to the tensile strength of 75% yield strength and 100% yield strength respectively to simulate the sea water with saturated H_2S and CO_2 solution with PH 3.5. The two groups of samples were not corroded or damaged after testing for 30 days in 400°F (204°C).

Gas	Temperature ℉(℃)	Corrosion rate mpy(mm/y)
Sulfur dioxide (dry)	70(21)	Nil
Sulfur Dioxide (water saturated)	70(21)	<0.1(<0.003)
Hydrogen sulfide (water saturated)	70(21)	<5(<0.127)

Table 1: Corrosion of Unalloyed Titanium by sulfur-containing Gases

The Material Handbook [2] also described the corrosion resistance of titanium in H_2S, and considered that the only fatal impact of H_2S on titanium was hydrogenation, which was only in contact with specific metals such as stainless steel, H_2S will promote hydrogenation. However, as long as the contact couples do not form, even if the aqueous solution contains H_2S, no galvanic corrosion occurs.

Based on the preceding theories, we developed a new type of (α+β) titanium alloy, which improves the internal structure and performance by adding several other metals to meet the application requirements of 25 years of life in high-corrosion areas. It is found that this kind of material has excellent corrosion resistance and can be used in the sea area with H_2S concentration as high as 15μg/g. This paper describes the corrosion test results of two kinds of titanium alloy materials with different alloy content and a common stainless steel material in high concentration H_2S. The experimental results reveal the application feasibility of special titanium alloy material in special sea area, especially high H_2S sea area.

2. EXPERIMENTAL PART

In order to verify the corrosion resistance of titanium alloy samples in saturated H_2S sea water, several samples were immersed to the simulated sea water. Prepare 65.5520 grams of sodium chloride (NaCl), 3.8522 grams of Ammonium chloride (NH_4Cl), 3.9162 grams of Sodium dihydrogen phosphate (NaH_2PO_4). Put them into 4 liters of deionized water and then adjust the PH to 7.7 using hydrogen chloride (HCl) solution of 1mol/L. After the solution is configured, move the solution into the oxygen removal device, and use nitrogen 200ml/min to remove oxygen 2h. Finally, inject H_2S gas at the flow speed of 200ml/min for 3h until saturation. Increases the water bath temperature to 30°C and adjusts the H_2S gas flow to 10ml/min. Put the test samples into configured solution and record the time. All samples taken out after 720h were subjected to complete surface characterization by scanning electron microscopy (SEM) and energy dispersive spectrometer (EDS). The surface composition was analyzed using EDS.

In this test, we choose two kinds of materials including 3 pcs (α+β) titanium alloy samples (sample 1-3#), 3pcs stainless steel samples (sample 4-6#). Dimensions of All samples are listed in table2.

Materials	Length a/mm	Width b/mm	Thickness c/mm	Hole inner diameter d/mm	Surface area /cm2
	50.11	25.21	2.77	5.31	29.00

Sample1-3#	50.17	25.14	2.87	5.24	29.12
	49.99	24.56	2.85	6.28	28.19
Sample 4-6#	49.92	24.79	10.12	6.02	24.18
	49.89	24.76	10.12	6.01	24.14
	49.87	24.76	10.15	6.01	24.13

Table 2: Test samples

3. RESULTS AND DISCUSSION

As illustrated in Figure 1, the macroscopic morphology showed no difference in the elemental distribution found on the points of titanium samples. But bubbles on the coating surface of stainless steel specimens were found.

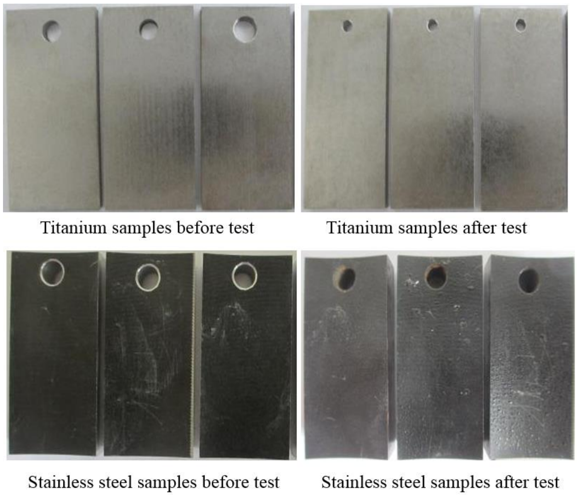

Figure 1: Graph of macroscopic morphology before and after the experiment

Figure 2 show the microstructure of titanium alloy samples before and after the 720h immersion test in the saturated sulfide simulation water solution. It can be seen from the SEM pictures of 1000 times that there are many grooves on the surface of the sample before the test, which is caused by machining. After the test, no corrosion points are found on the surface of the sample. There was no obvious corrosion on the surface of the two kinds of titanium alloy.

As shown in the SEM photos of 1000 times of the stainless steel coating, the coating surface is dense, and some bright white areas exist, which are caused by mechanical damages. After the test, there are bubbles on the surface of the coating, in addition, the surface of the coating is loose, which indicates that the performance of the stainless steel coating deteriorates under the condition of this test.

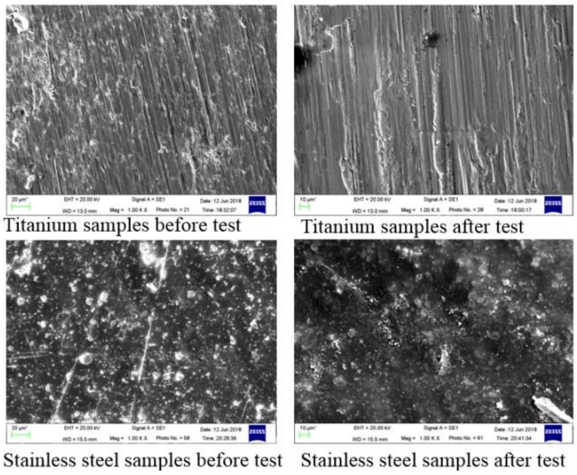

Figure 2: Macroscopic morphology before and after test in simulated sea water for 72h

Figure 3 shows the EDS results of two kinds of titanium alloy samples before and after 720h immersion test in saturated hydrogen sulfide water solution. According to Table 6, the EDS components of the two titanium alloys before and after the test are mainly Ti, V, Al, C and there is no obvious change.

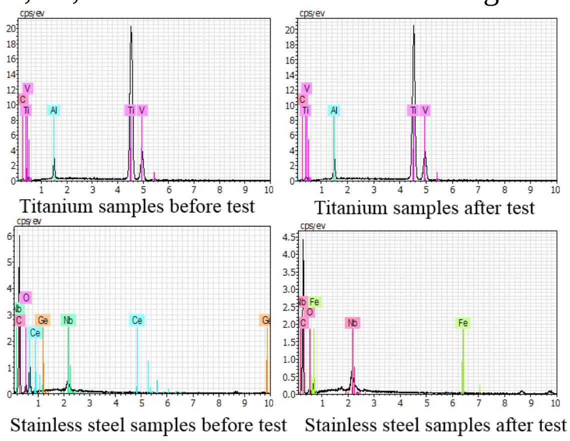

Figure 3: EDS before and after test in simulated sea water for 720h

In Figure 3, it can be seen that the main components of the stainless steel coating before the test are C, O, and Nb, including trace Ge and Ce. After the test, the main components of the stainless steel coating are C, O, and Nb, the new element Fe appeared, indicating that the coating was damaged and the surface formed micropores.

The corrosion rate of four samples was calculated by weight-loss method. The corresponding formula is listed as follows:

$$X = \frac{(W_1 - W_2) \times 87600}{A \times T \times D} \quad mm/a \qquad (4)$$

Where, X- Corrosion rate (mm/a), W_1, W_2-weight before and after test, g; A-surface area, cm^2; T-test time, h; D-density, g/cm^3.

As shown in Table 3-4, the average corrosion rate of the two titanium alloys is 0 mm/a, and the average corrosion rate of the stainless steel is 0.0003 mm/a. Obviously, the stainless steel has corroded, and the titanium alloy has no any change.

Samples	Weight before test/g	Weight after test/g	Loss weight/g	Corrosion rate m/a	Average corrosion rate mm/a
Sample 1-3#	15.2787	15.2787	0	0	0
	15.7860	15.7860	0	0	
	15.5177	15.5177	0	0	

Table 3: Corrosion rate of titanium alloy samples

Sample	Weight before test/g	Weight after test/g	Loss weight/g	Corrosion rate m/a	Average corrosion rate mm/a
Sample 4-6	96.2119	96.2111	0.0008	0.0005	0.0003
	96.2752	96.2747	0.0005	0.0003	
	96.3614	96.3612	0.0002	0.0001	

Table 4: Corrosion rate of stainless steel samples

4. CONCLUSION

In this paper, the corrosion resistance of several titanium alloy samples in simulated high H_2S seawater are studied mainly from theoretical analysis and simulation experiments. The results show that the hydrogen embrittlement of titanium RPT and BU takes far more than 25 years in seawater, even in highly corrosive seawater.
In addition, the RPT and BU are deployed on the seabed and are not subjected to tensile stress. Therefore, no stress corrosion or fracture occurs on RPT and BU at the bottom of the sea.

The titanium alloy materials were soaked for 30 days without any corrosion or damage in an oxygen-free, high-concentration H_2S solution with PH3.5.
As described as before, the titanium alloy RPT and BU will not corrode in the Black Sea environment, and will not cause any catastrophic corrosion or damage.

5. REFERENCES

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