

HYDROGEN ABSORPTION OF TITANIUM IN OFFSHORE RELATED ENVIRONMENTS UNDER CATHODIC CHARGING

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Abstract

Titanium alloys of Grade 2, 5, 9, 12 and Beta-C have been exposed for periods up to two years with cathodic polarization in deaerated artificial seawater at temperatures between 20 and 80 °C. All alloys except Grade 12 had low hydrogen absorption at -1050 mV vs. Ag/AgCl. Titanium Grade 12 had a hydrogen absorption 3-20 times higher than the other alloys, and is not recommended for use in applications where the material is exposed to cathodic protection. The high absorption rate was related to the nickel content of this alloy. The alpha-beta high-strength alloys Grade 5 (6Al-4V) and Grade 9 (3Al-2.5V) showed about the same hydrogen absorption as unalloyed titanium Grade 2. The high-strength beta alloy Beta-C had generally somewhat higher hydrogen absorption than unalloyed titanium, but lower than Grade 12.

The hydrogen absorption in titanium Grade 12 was considerably lower at -700 mV than at -1050 mV vs. Ag/AgCl. In the other alloys the hydrogen absorption was low at both these potentials. The hydrogen absorption in deaerated seawater was about the same at 20 °C and 80 °C. The reason for this is that surface films containing carbonates form at higher temperatures, and these films seem to protect against hydrogen absorption. This effect is even stronger in water containing carbon dioxide, where carbonate films form at lower temperatures.

Introduction

Titanium has an excellent corrosion resistance in seawater, and has been widely used for seawater cooled heat exchangers for the last twenty years. There is a growing interest for titanium also in other offshore applications, where titanium often will be coupled to other materials and may also be exposed to cathodic protection systems. In some of these applications the low weight-to-strength ratio makes titanium especially attractive, particularly in combination with its low modulus of elasticity. A 400 m long titanium drilling riser is currently being evaluated for a tension leg platform in the North Sea, and a titanium stress joint has been in service at 500 m water depth in the Gulf of Mexico. Here the titanium components are large diameter (~30 inch) tubes of high strength titanium with thick wall (1 inch). This type of applications requires the use of high-strength titanium alloys of the alpha-beta or beta type.

Titanium alloys absorb hydrogen at low potentials, and when the solubility limit is exceeded hydrides will form. The hydrides are brittle and in extreme cases hydrides may lead to deterioration or fracture of the component. The behaviour of alpha titanium alloys in seawater is apparently well documented, while little information is available on the hydrogen absorption behaviour of high strength alloys. It is often difficult to use hydrogen absorption data because hydrogen analyses have been applied without differentiation between hydride films at the surface and hydrogen absorbed in the bulk material. It is mainly precipitated hydrides in the interior of the metal that will endanger the service life of a component, while thin hydride films at the surface have less practical implications.

The most important factors for hydrogen absorption in titanium are pH, electrochemical potential, temperature and alloy composition. Rules of thumb given for seawater service of alpha titanium alloys are not always reliable, and they can not be applied for beta or alpha-beta alloys. Information relevant to conditions on the hydrocarbon side of oil and gas production or transport equipment is lacking. Experience from oil refineries shows that coupling to carbon steel has led to hydrogen absorption in environments containing hydrogen sulphide. An important question is whether the small H_2S amounts present in North Sea hydrocarbons (<100 ppm) are enough to trigger hydrogen absorption.

The objective of the present work was to investigate hydrogen absorption on the seawater side in titanium components coupled to other metals exposed to cathodic protection and on the hydrocarbon side of titanium components coupled to carbon steel. The experiments were a part of an EEC funded project within the EURAM programme (1). The project was based on a co-operation between research institutions in four European countries, including Inasmet, Spain, Technical Research Institute of Finland, Imperial College, England and Institutt for energiteknikk, Norway. The aim of the Norwegian studies was to investigate hydrogen absorption without mechanical loading, while work in Finland and Spain was concentrated on the influence of cathodic protection on stress corrosion cracking and corrosion fatigue in artificial seawater. The British studies were aimed at the role of hydrides in the cracking of titanium alloys.

Experimental

Hydrogen absorption studies were performed with the following titanium alloys: Ti Grade 2 (CP Ti), Grade 5 (6Al-4V), Grade 9 (3Al-2.5V), Grade 12 (0.8Ni-0.3Mo) and Beta-C. In some of the experiments new experimental alloys supplied by TIMET (Beta-21S) and Sumitomo (0.05Pd-0.3Co) were included. The composition and mechanical properties of the alloys are given in Table I. Flat specimens with thickness 3 mm and surface area about 5 cm² were exposed to synthetic seawater according to ASTM D-1141 in glass cells with automatic pH and temperature control. The electrolyte was replaced at regular intervals. The specimens were ground and then pickled in a HNO_3 -HF- H_2O solution before the experiment. Experiments were performed at 20, 40, 60 and 80 °C. The solution was flushed with either N_2 , CO_2 , or CO_2 with 50 ppm H_2S in order to simulate either produced water (hydrocarbon environment with CO_2) or seawater at large depths where the oxygen content is low. The pH of the solution was kept at 4.0 in most experiments, while a few experiments were performed with higher pH values. The potential of the specimens was kept at either -700 mV vs. Ag/AgCl (corresponding to galvanic coupling to carbon steel) or -1050 mV vs. Ag/AgCl (corresponding to a structure with cathodic protection). Exposure times were from 20 to 700 days. The specimens were examined for hydride precipitation by metallography, and the hydrogen content of both exposed and unexposed specimens was measured by TIMET by vacuum extraction and mass spectrometry.

Table I. Chemical composition and mechanical properties of the investigated alloys. Data from certificate for all alloys except Grade 9.

Composition %	Alloy						
	2	5	9	12	0.05Pd-0.3Co	Beta-C	Beta-21S
N	0.008	0.01	0.02	0.003	0.05	0.017	
C	0.025	0.02	0.18	0.016	0.10	0.2	
Fe	0.05	0.22	0.25	0.12	0.07	0.08	
O	0.19	0.125	0.15	0.14	0.20	0.077	
Al		6.2	2.5-3.5			3.3	3
V		4.0	2-3			8.0	
Other				Mo 0.28	Pd 0.03-0.07	Mo 4.0	Mo 15
				Ni 0.87	Co 0.2-0.7	Zr 3.9	Nb 2.6
						Cr 6.4	Si 0.2
H * ppm	70	60	80	50	50	140	90
Mechanical properties							
YP MPa	418	986	560	400		834	
UTS MPa	527	1034	655	600		862	
Elongation %	26	13	29	23		21	

* Measured by TIMET for this project

Results

The amount of absorbed hydrogen in the different titanium alloys exposed to artificial seawater with CO₂ at 80 °C, pH 4.0 and -1050 mV vs. Ag/AgCl is shown in Figure 1. The hydrogen data are given as absorbed hydrogen in μg per mm² surface area of the specimen. This parameter gives values for absorbed hydrogen independent of the thickness of the material. Hydrogen values in ppm of the bulk material are less informative and do not take into account that most

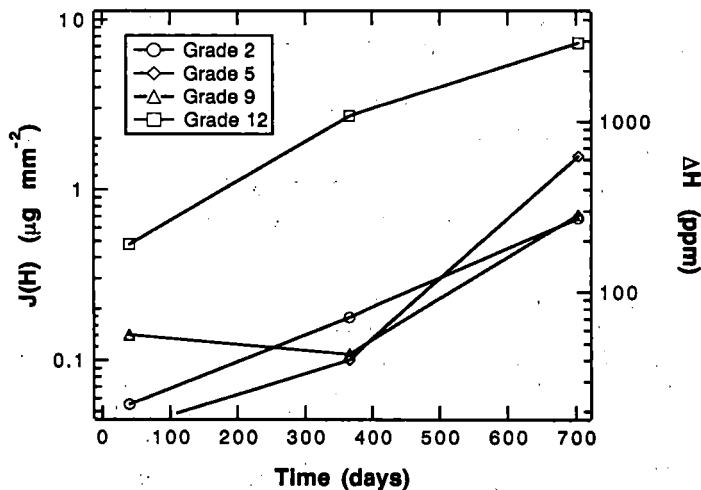


Figure 1. Hydrogen absorption in titanium as function of exposure time. Exposure in artificial seawater with CO₂ at 80 °C, -1050 mV vs. Ag/AgCl and pH 4.0.

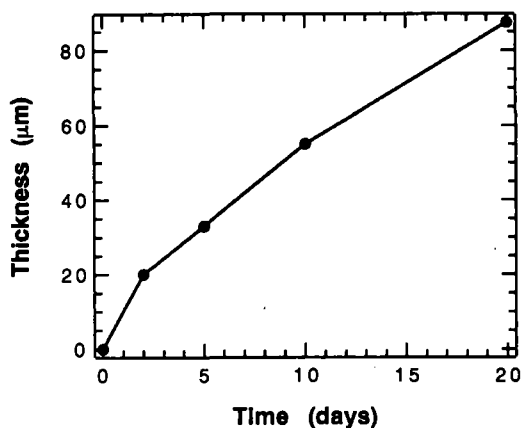


Figure 2. Thickness of hydride layer in titanium Grade 12 as function of exposure time. Exposure in artificial seawater with CO_2 at 80°C , -1050 mV vs. Ag/AgCl and $\text{pH } 4.0$.

considerable hydride formation, while very little hydrides were found in the other alloys. The thickness of the hydride layer in Ti Grade 12 specimens tested at 80°C , $\text{pH } 4.0$ and -1050 mV vs. Ag/AgCl is shown as function of exposure time in Figure 2. The figure shows that an appreciable hydride layer can be observed already after two days' exposure. The thickness of the layer increases approximately proportionally with the square root of the exposure time.

Experiments with abraded and pickled specimens tested with nitrogen flushing at 20°C showed that abraded specimens had considerably higher hydrogen absorption than pickled specimens after 40 days' exposure. After 120 days' exposure the difference between pickled and abraded specimens was much smaller, and the initial surface condition seems to be less important.

The effect of temperature on the hydrogen absorption in the different alloys is shown in Figure 3. In the experiments with nitrogen flushing the hydrogen absorption increases markedly from 20°C to 40°C and then decreases from 40 to 80°C . In experiments with CO_2 flushing the hydrogen absorption decreases from 20 to 40°C and then remains about the same up to 80°C . Grade 12 has the highest hydrogen absorption at all temperatures, while Beta-C also absorbs much hydrogen at 20 and 40°C .

The hydrogen absorption in Ti Grade 12 after one year exposure in synthetic seawater with CO_2 flushing at 80°C and $\text{pH } 4.0$ was about seven times higher at -1050 mV than at -700 mV vs. Ag/AgCl . For the other alloys the hydrogen absorption was much lower, with almost no difference between -700 and -1050 mV vs. Ag/AgCl . An experiment with $\text{CO}_2 + 50\text{ ppm H}_2\text{S}$ as flushing gas with $\text{pH } 6.5$ resulted in similar or somewhat lower hydrogen uptake than pure CO_2 and $\text{pH } 4.0$. A few experiments with different pH values were performed with nitrogen flushing at 80°C and -1050 mV vs. Ag/AgCl . Grade 12 specimens tested at $\text{pH } 13$ showed no hydride precipitation, while $\text{pH } 6.2$ resulted in formation of some hydrides. Specimens exposed at $\text{pH } 4.0$ under the same conditions showed a thick hydride layer at the surface and hydride needles deep into the metal.

of the absorbed hydrogen is accumulated in a thin surface layer. However, as many previously reported hydrogen data have been given in ppm, an approximate scale for the hydrogen content in ppm in a 3 mm thick plate exposed on both sides is also given in the figure. The hydrogen content in ppm will be different for other thicknesses.

Figure 1 shows that the hydrogen absorption does not slow down even after long exposure times. In fact, the hydrogen values after two years are more than twice the values after one year for all alloys. The figure also shows that Ti Grade 12, which contains nickel and molybdenum, absorbs 3-20 times more hydrogen than Grade 2, 5 and 9. Grade 12 showed

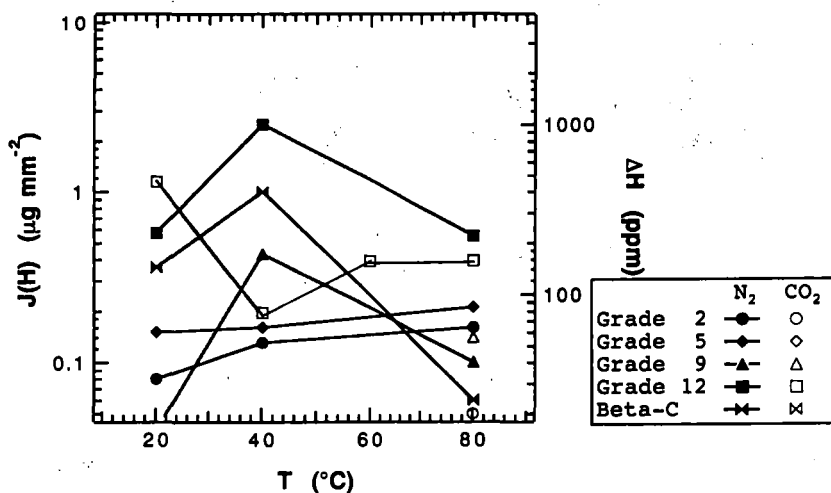


Figure 3. Hydrogen absorption in titanium as function of temperature. 40 days' exposure in artificial seawater at -1050 mV vs. Ag/AgCl and pH 4.0.

Discussion

Effect of temperature and water chemistry

Hydrogen absorption in titanium has traditionally been considered to be a problem only at temperatures above 80 °C, where the diffusion rate of hydrogen becomes significant (2). The present experiments in synthetic seawater with nitrogen flushing show that the hydrogen absorption increases from 20 to 40 °C, but then decreases from 40 to 80 °C. With CO₂ flushing the hydrogen absorption decreases already from 20 to 40 °C. The surface films on titanium seem to be more important for the total hydrogen absorption than the effect of temperature on diffusion. An X-ray energy dispersive analysis of the surface of specimens exposed with nitrogen flushing at 80 °C showed the presence of calcium that has been deposited on the surface, probably as CaCO₃. Carbonate scales form easily at high temperature because the solubility of calcium carbonate decreases with increasing temperature. Natural seawater contains enough carbonate ions to get this effect. When the water contains carbon dioxide, the content of carbonate ions is larger and carbonate scales are more easily formed at low temperature. This accounts for the observed effect of CO₂ on the hydrogen absorption. The effect of carbonate films on hydrogen absorption of titanium in seawater may have important practical consequences, as this might result in negligible hydrogen absorption in cases where this otherwise could be a problem.

Previous investigations of grade 2 titanium in natural seawater showed small differences in hydrogen absorption between 25 and 50 °C, while exposure at 80 °C gave a marked increase in hydride layer thickness (3). These results were obtained at pH 2 and are not relevant for normal seawater exposure. Another study reported a higher hydrogen absorption in 3 months at 25 °C compared to two months at 100 °C (4). This is more in line with the present findings.

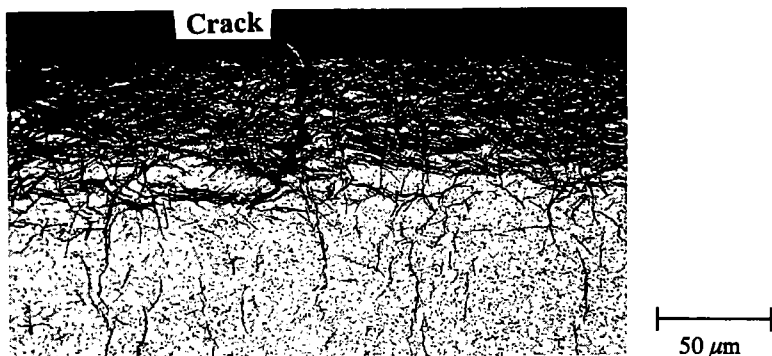


Figure 4. Hydride layer with crack on titanium Grade 12 after 40 days' exposure in artificial seawater with CO_2 at 80 °C and pH 4.0.

In order to judge the detrimental effect of hydrogen it is necessary to have information on the distribution of hydrides as well as the total hydrogen content. Hydrides oriented perpendicular to the loading direction can be dangerous even with reasonably low total hydrogen contents. This is clearly demonstrated in Figure 4 where surface cracks starting from hydrides can act as stress risers by introducing a stress concentration factor.

Dense surface hydride layers were observed in Grade 2 specimens exposed with nitrogen flushing at 20 °C and almost no hydrides at 80 °C, although the hydrogen content was about the same at the two temperatures. In Grade 12 specimens exposed with CO_2 flushing, dense surface hydrides with thickness 5-30 μm were observed in specimens exposed at 20 °C, while specimens exposed at 80 °C also showed hydride needles up to 300 μm deep into the metal. Specimens exposed at 40 and 60 °C had thicker surface hydride layers with up to 60 μm depth. This may seem surprising since the hydrogen absorption was highest at 20 °C, as shown by the open points in Figure 3. However, the hydride layer at 20 °C was very dense because very little of the absorbed hydrogen had diffused into the bulk metal. These observations illustrate that the diffusion of hydrogen from the surface and deeper into the metal increases with temperature, but this is not the limiting factor for the hydrogen absorption.

The hydrogen absorption increases with decreasing pH. The experiments with pH 4 represent accelerated conditions compared to neutral seawater. Flushing with CO_2 + 50 ppm H_2S at pH 6.5 gave similar or somewhat lower hydrogen uptake than pure CO_2 at pH 4.0. This does not exclude a detrimental effect of H_2S on hydrogen absorption, but it seems that the small amounts of hydrogen sulphide in the North Sea fields (<100 ppm) do not cause any dramatic changes in the hydrogen absorption for the hydrocarbon side of titanium components coupled to carbon steel.

Effect of alloying elements

Titanium Grade 12 absorbed much more hydrogen than the other alloys (3-20 times more), and was the only alloy with extensive hydride formation. Small amounts of nickel are known to cause increased hydrogen absorption in titanium alloys (5), and it is likely that the 0.8 % nickel in Grade 12 accounts for the increased hydrogen absorption. This was verified by Ti Grade 2 specimens with small amounts of nickel electrodeposited on the surface. These specimens

developed a severe hydride attack after only 20 days' exposure, while no hydrides were found in parallel specimens without nickel. A few experiments with the alloy Ti 0.05Pd-0.3Co showed two to three times higher hydrogen absorption than for unalloyed titanium Grade 2. The palladium content is probably responsible for this, but the cobalt content may also contribute.

The high-strength beta alloy Beta-C showed generally somewhat higher hydrogen absorption than unalloyed titanium, but lower than Grade 12. The alloy Beta-21S was also tested and had about the same hydrogen absorption as Beta-C. Both the solubility and the diffusion rate of hydrogen are several times higher in the beta alloys than in the alpha alloys, and no hydrides were ever found in the beta alloys.

The alpha-beta high-strength alloys Grade 5 (6Al-4V) and Grade 9 (3Al-2.5V) had about the same hydrogen absorption as unalloyed titanium Grade 2. However, Grade 9 had higher hydrogen absorption in a pickled specimen at 40 °C and an abraded specimen at 20 °C. No hydrides were found in the alpha-beta alloys, except for the abraded Grade 9 specimen mentioned above, where a 100 μm thick hydride layer was found after 40 days' exposure.

Effect of potential

The hydrogen absorption in titanium Grade 12 was considerably lower at -700 mV than at -1050 mV vs. Ag/AgCl. In the other alloys the hydrogen absorption was low at both these potentials. This together with the beneficial effect of CO_2 indicates that hydrogen absorption should not be a problem on the hydrocarbon side of titanium components coupled to carbon steel, where the potential is typically -700 mV vs. Ag/AgCl. On the seawater side, a titanium component coupled to a structure with cathodic protection will have a potential of about -1050 mV vs. Ag/AgCl. At this potential significant hydrogen absorption can occur in titanium Grade 12. Previous investigations have indicated that hydrogen absorption occurs in natural seawater only when titanium has a potential lower than about -0.7 V vs. SCE, with significant hydrogen absorption between -0.8 and -1.0 V vs. SCE (6, 7). Other investigators have found significant hydriding of titanium in neutral seawater only at potentials lower than -1.2 V vs. SCE, and they have suggested -1.0 V vs. SCE as a limit for avoiding significant hydriding below 45 °C (8).

Conclusions

Exposure of titanium alloys of Grade 2, 5, 9, 12 and Beta-C in deaerated artificial seawater at -1050 mV vs. Ag/AgCl showed a low but significant hydrogen absorption in all alloys except Grade 12. The exposure at pH 4 represents accelerated conditions compared to neutral seawater. The hydrogen absorption did not slow down even after two years. Titanium Grade 12 had a hydrogen absorption 3-20 times higher than the other alloys and extensive hydride formation. This alloy should not be recommended for use in applications where the material is exposed to cathodic protection. The high absorption rate of Grade 12 is related to the nickel content. The alpha-beta high-strength alloys Grade 5 (6Al-4V) and Grade 9 (3Al-2.5V) showed about the same hydrogen absorption as unalloyed titanium Grade 2. The high-strength beta alloy Beta-C had somewhat higher hydrogen absorption than unalloyed titanium, but lower than Grade 12. No hydrides were found in the Beta-C alloy. The results indicate that these high-strength alloys are at least as good as unalloyed titanium regarding hydrogen absorption.

The hydrogen absorption in deaerated seawater was about the same at 20 °C and 80 °C, while it was higher at 40 °C. The reason for this is that surface films containing carbonates start to form between 40 °C and 80 °C. These films seem to protect against hydrogen absorption. This

effect is even stronger in water containing carbon dioxide, where the hydrogen absorption decreases from 20 to 40 °C because carbonate film formation start at lower temperatures.

The hydrogen absorption is initially much higher at abraded surfaces than at pickled surfaces, but the differences in original surface conditions become less important after longer exposure times. The hydrogen absorption in titanium Grade 12 was considerably lower at -700 mV vs. Ag/AgCl than at -1050 mV vs. Ag/AgCl. This together with the beneficial effect of CO₂ indicates that hydrogen absorption should not be a problem on the hydrocarbon side of titanium components even with small contents of H₂S, while some hydrogen absorption may occur on the seawater side of titanium components coupled to a structure with cathodic protection.

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