COMPATIBILITY OF MATERIALS WITH HYDROGEN PARTICULAR CASE: HYDROGEN ASSISTED STRESS CRACKING OF TITANIUM ALLOYS.

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ABSTRACT

A review of the effect of hydrogen on materials is addressed in this paper. General aspects of the interaction of hydrogen and materials, hydrogen embrittlement, low temperature effects, material suitability for hydrogen service and materials testing are the main subjects considered in the first part of the paper. As a particular case of the effect of hydrogen in materials, the hydride formation of titanium alloys is considered. Alpha titanium alloys are considered corrosion resistant materials in a wide range of environments. However, hydrogen absorption and the possible associated problems must be taken into account when considering titanium as a candidate material for high responsibility applications. The sensitivity of three different titanium alloys, Ti Gr-2, Ti Gr-5 and Ti Gr-12, to the Hydrogen Assisted Stress Cracking phenomena has been studied by means of the Slow Strain Rate Technique (SSRT). The testing media has been sea water and hydrogen has been produced on the specimen surface during the test by cathodic polarization. Tested specimens have been characterized by metallography and scanning electron microscopy. Results obtained show that the microstructure of the materials, particularly the β phase content, plays an important role on the sensitivity of the studied alloys to the Hydrogen Assisted Stress Cracking Phenomena.

1.0 INTRODUCTION. COMPATIBILITY OF MATERIALS WITH HYDROGEN

All materials deform under load. Ductility is the ability to deform permanently prior to fracture.

Most materials behave linearly under low loads. A material is elastic if, after being elongated under stress, it returns to its original shape as soon as the stress is removed [1].

At a certain strain, when the load exceeds the yield load called 'yield stress', the stress strain behaviour becomes non-linear. Behaviour is not reversible, i.e. permanent changes in shape occur, but the volume remains constant. A further increase of the strain eventually reaches the ultimate load called 'ultimate tensile stress' beyond which the stress decreases finally leading to rupture.

Ductile materials can accommodate local stress concentrations, they can be greatly bent and reshaped without breaking. In contrast, brittle materials have only a small amount of elongation at fracture.

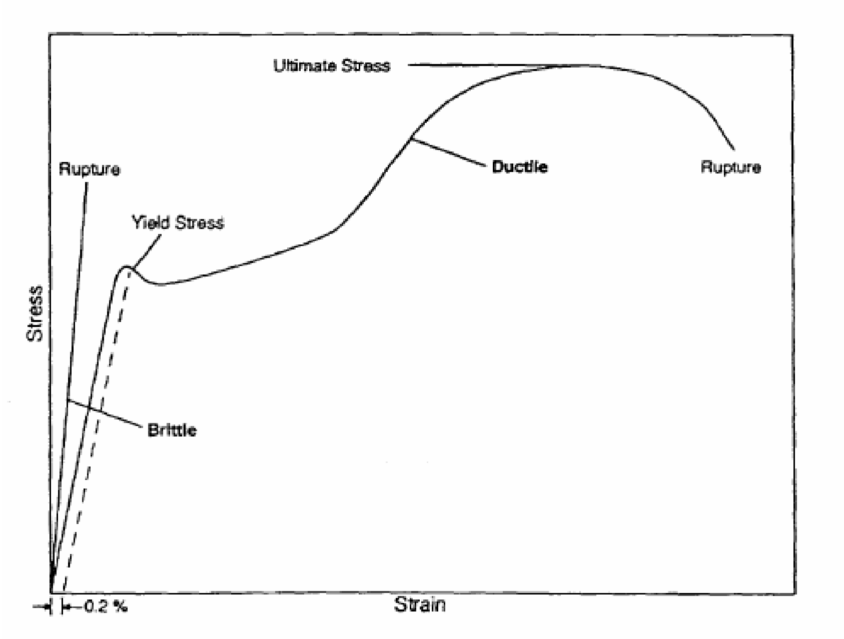

Figure 1: Ductile and brittle behaviour [2]

Hydrogen can have two main damaging effects on materials:

- *Low temperature effect*. At low temperature for example when it is stored in liquid form it can have an indirect effect called “cold embrittlement”. This effect is not specific to hydrogen and can occur with all the cryogenic gases if the operating temperature is below the ductile-brittle transition temperature.

Cryogenic temperatures can affect structural materials. With decreasing temperature, there is a decrease in toughness that is very slight in face centred cubic materials, but can be very marked in body centre cubic ones such as ferritic steels. Metals that work successfully at low temperatures include aluminium and its alloys, copper and its alloys, nickel and some of its alloys, as well as stable austenitic stainless steels.

- *Hydrogen embrittlement*. Hydrogen can have a direct effect on the material by degrading its mechanical properties; this effect is called “hydrogen embrittlement” and is specific to the action of hydrogen and some other hydrogenated gases.

The effect of hydrogen on material behaviour, on its physical properties, is a fact. Hydrogen may degrade the mechanical behaviour of metallic materials and lead them to failure.

Hydrogen embrittlement affects the three basic systems of any industry that uses hydrogen: Production, Transport/Storage and Use.

When tensile stresses are applied to a hydrogen embrittled component, it may fail prematurely in an unexpected and sometimes catastrophic way. An externally applied load is not required as the tensile stresses may be due to residual stresses in the material. The threshold stresses to cause cracking are commonly below the yield stress of the material. Thus, catastrophic failure can occur without significant deformation or obvious deterioration of the component. [3]

It can take place in three different ways:

- *Internal Hydrogen Embrittlement*. Takes place when hydrogen enters the metal during its processing. It is a phenomenon that may lead to the structural failure of material that never has been exposed to hydrogen before. Internal cracks are initiated showing a discontinuous growth. Not more than 0.1 - 10 ppm hydrogen in the average are involved. The effect is observed in the temperature range between 173 and 373 K and is most severe near room temperature.

- *External Hydrogen Embrittlement*. Occurs when the material is subjected to a hydrogen atmosphere, e.g. storage tanks. Absorbed and/or adsorbed hydrogen modifies the mechanical response of the material without necessarily forming a second phase. The effect strongly depends on the stress imposed on the metal. It also maximizes at around room temperature.

- *Hydrogen Reaction Embrittlement*. It is a phenomenon in which the hydrogen chemically reacts with a constituent of the metal to form a new microstructural element or phase such as a hydride or to generate methane gas bubbles by reaction with the carbon that accumulates in the grain boundaries of metallic components leading to failure caused by void growth and assisted by creep.

The case of hydride formation presents a different nature and that of titanium alloys is a typical one. The microstructure of these alloys consists usually of two phases (α and β) with different hydrogen solubilities and diffusivities. Hydrogen enters the alloy via grain boundaries or other easy paths as β phase, forming hydrides that precipitate in the α phase.

This particular case of the hydride formation in titanium alloys is the considered in this paper.

2.0 EXPERIMENTAL

2.1 Materials

The studied materials have been the alpha titanium alloys Ti Gr-2, Ti Gr-5 and Ti Gr-12 (ASTM B-265) [4], hot rolled and annealed. Their chemical composition is given in table 1.

Table 1. Chemical composition of studied titanium alloys (weight %).

Alloy	N	C	H	O	Fe	Al	V	Mo	Ni	Ti
Ti Gr-2	0,003	0,005	0,003	0,126	0,048	-	-	-	-	bal.
Ti Gr-5	0,011	0,020	0,008	0,144	0,18	6,4	3,8	-	-	bal.
Ti Gr-12	0,017	0,010	0,002	0,150	0,11	-	-	0,26	0,66	bal.

2.2 Test conditions and experimental set-up

The sensitivity of the studied materials to Hydrogen Assisted Stress Cracking (HASC) has been studied by means of the Slow Strain Rate Technique (SSRT).

The experiments were carried out using constant extension rate tensile testing machines of 50 kN capacity and selectable crosshead speed within the range of 0.1 to 10^{-6} mm/s.

Round tensile test specimens were located in Hastelloy C-276 autoclaves and attached to a fixed frame by one end and to the pull rod by the other.

Fittings made of ZrO_2 were used to ensure the electrical insulation of the specimens from the autoclave (Figure 2).

Figure 2. General view of the SSRT equipment. Detail of testing specimen in the autoclave.

Specimens were tested in a sea water at strain rates ranging from 10^{-4} s^{-1} to 10^{-7} s^{-1}, temperatures of 90 and 170 ºC, and an argon pressure of 10 bar. In order to be able to compare the results obtained in sea water, additional tests were also carried out in argon as an inert medium.

Once the test specimen was attached, autoclaves were filled either with sea water or argon, closed, pressurized and heated; when testing temperature and pressure were reached, the specimens were pulled until fracture at the selected actuator displacement speed.

In tests with applied polarization, hydrogen was cathodically produced on the specimen surface using a potentiostat. The specimen was located in the autoclave together with the reference (Ag/AgCl) and counter (platinum) electrodes, -1000 and -1500 mV (Ag/AgCl) being the applied potentials. Tests were performed at 90ºC and a strain rate of 10^{-6} s^{-1}. Great care was taken to avoid shorting of electrical connections.

Load, position of the actuator, time and temperature data were continuously logged during the test by means of the microprocessor that controlled the testing machine. After each test, the elongation, reduction of area, energy, yield strength, maximum load, and true stress at fracture were the measured parameters to assess the loss of ductility and sensitivity of the studied materials to the HASC. This was complemented by metallographic studies performed by optical microscopy on probes prepared from longitudinal cuts of the tested specimens (Figures 4, 5 and 6), and fractographic studies of the fracture surface of the specimens by scanning electron microscopy (Figure 3).

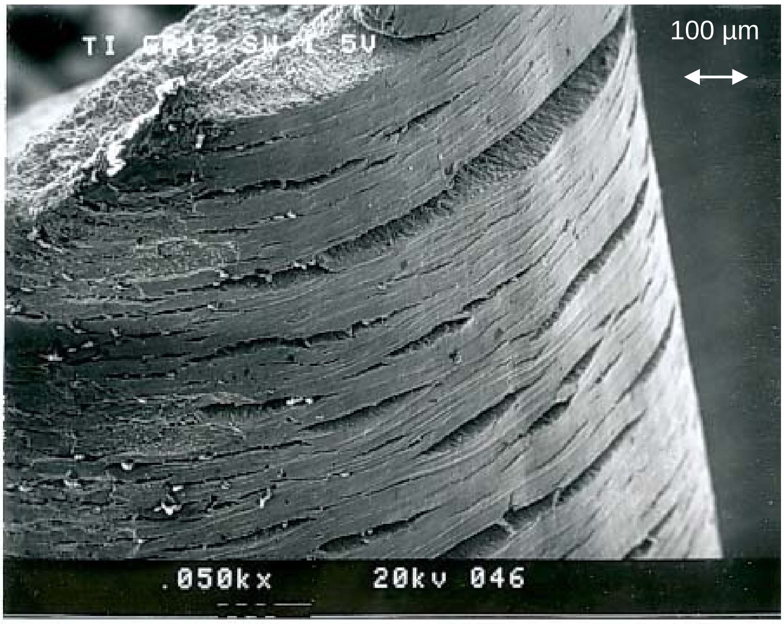

Figure 3. Secondary cracking on lateral surface of Ti Gr-12 specimen tested at a strain rate of 2x10-7 s-1 in sea water with a cathodic polarization of -1500 mV (Ag/AgCl).

Figure 4. Hydride layer and secondary cracks on lateral surface of Ti Gr-12 specimen tested at a strain rate of 2x10-7 s-1 in sea water with a cathodic polarization of -1500 mV (Ag/AgCl).

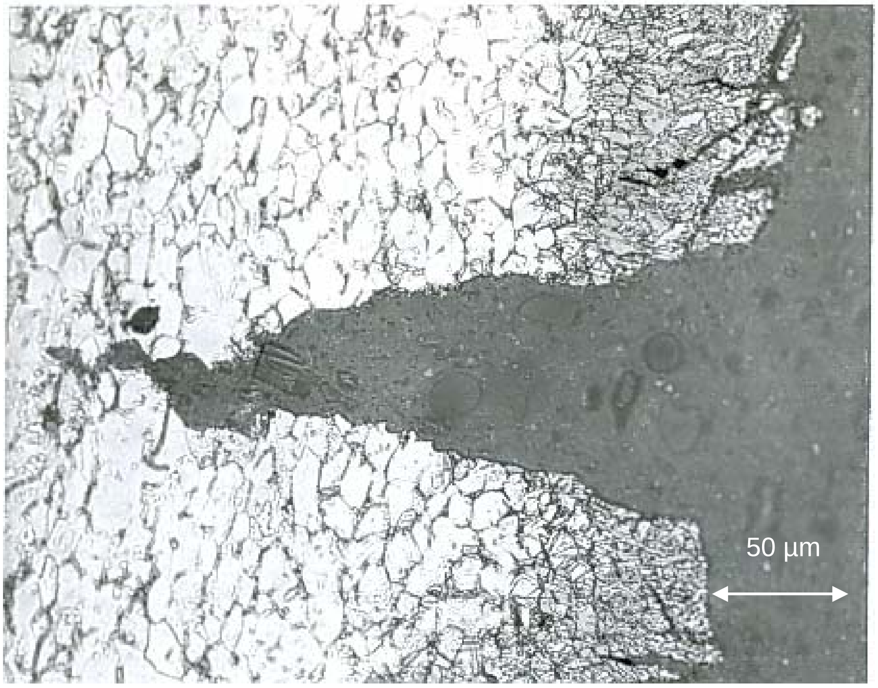

Figure 5. Hydride layer and secondary cracks on lateral surface of Ti Gr-12 specimen tested at a strain rate of 2x10-7 s-1 in sea water with a cathodic polarization of -1500 mV (Ag/AgCl).

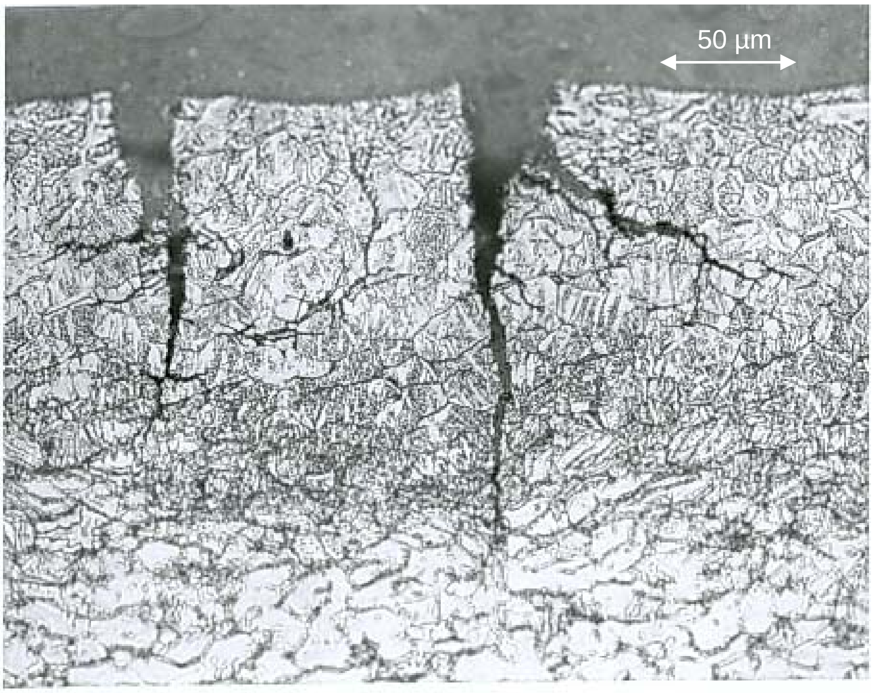

Figure 6. Hydride layer and secondary cracks on lateral surface of Ti Gr-12 specimen tested at a strain rate of 2x10-7 s-1 in sea water with a cathodic polarization of -1500 mV (Ag/AgCl).

3.0 RESULTS

No loss of ductility was noticed for Ti Gr-2 and Ti Gr-5 alloys at any of the testing conditions, even in tests performed with cathodic polarization. No secondary cracks were observed in the metallographic studies and the fracture surface features did not change from tests performed in argon to those in sea water; in all cases a fully ductile fracture surface was observed.

The same was noticed in the case of Ti Gr-12 when tested in argon and sea water. But results changed for this alloy when cathodic polarization was used; in tests performed with -1000 mV, a slight loss of ductility was observed, this loss of ductility being manifested in the mechanical parameters of elongation and reduction of area of the specimen. When the applied cathodic polarization was of -1500 mV (Ag/AgCl), an important loss of ductility and secondary cracks due to hydride precipitation were observed. Figure 3 shows lateral surface cracking suffered by the specimen near the fracture zone. Figures 4, 5 and 6 show hydride channels penetrating from the surface of a Ti Gr-12 alloy specimen. These channels provided paths for the development of brittle cracks during straining.

The thickness of the titanium hydride layer formed on the specimen surface when tested in the highest cathodic pollarization condition, -1500 mV (Ag/AgCl), has resulted to be of up to 30 μm for the Ti Gr-2 alloy, 120 μm for the Ti Gr-12 alloy and has not been observed in the case of Ti Gr-5 alloy.

4.0 COMMENTS

The different SCC behaviour of the studied titanium alloys when cathodic polarization is applied, seems to be associated with the easy of penetration and solubility of hydrogen into the metal during slow straining. In order to explain this behaviour, the following aspects should be taken into account:

1. The solubility of hydrogen in the alfa phase at the eutectic temperature (300ºC) is of 6,72% atomic (1500 ppm); this solubility is of 39% atomic (13200 ppm) at the same temperature in beta phase [5].

2. The β-phase content is negligible for Ti Gr-2 alloy, approximately 3% volume for Ti Gr-12 [6] and 15% for Ti Gr-5 [7].

3. The diffusivity of hydrogen in titanium alpha phase is considerably lower than in the beta phase [8, 9]. A summary of diffusion data obtained in studies performed in different alloys are collected in Table 2.

Table 2. Hydrogen Diffusion in Titanium

Phase	Diffusion Coefficient ($cm^2.s^{-1}$)	Values at ($cm^2.s^{-1}$)		Ref.
		25ºC	80ºC	
α	$D\alpha = 6x10^{-2}.exp(-14400 \pm 800/RT)$	$3,2 \times 10^{-12}$	$1,4 \times 10^{-10}$	[8]
β	$D\beta = 1,58x10^{-3}.exp(-5140 \pm 300/RT)$	$3,3 \times 10^{-7}$	$1,1 \times 10^{-6}$	[9]

The short hydride layer produced and the absence of hydride induced secondary cracking on the Ti Gr-2 alloy can be explained by the low solubility and diffusivity of hydrogen in this fully alpha alloy. In the case of Ti Gr-12, the small amount of beta phase, is able to channel the hydrogen towards the bulk material increasing its penetration; when saturation of hydrogen is reached, hydrides precipitate in the alpha phase inducing cracking. (Figures 7 and 8) [10, 11, 12].

In the case of the Ti Gr-5 alloy, the beta phase content seems to be enough to dissolve the hydrogen produced on the specimen surface during the test, without producing nor hydride precipitation nor secondary cracking.

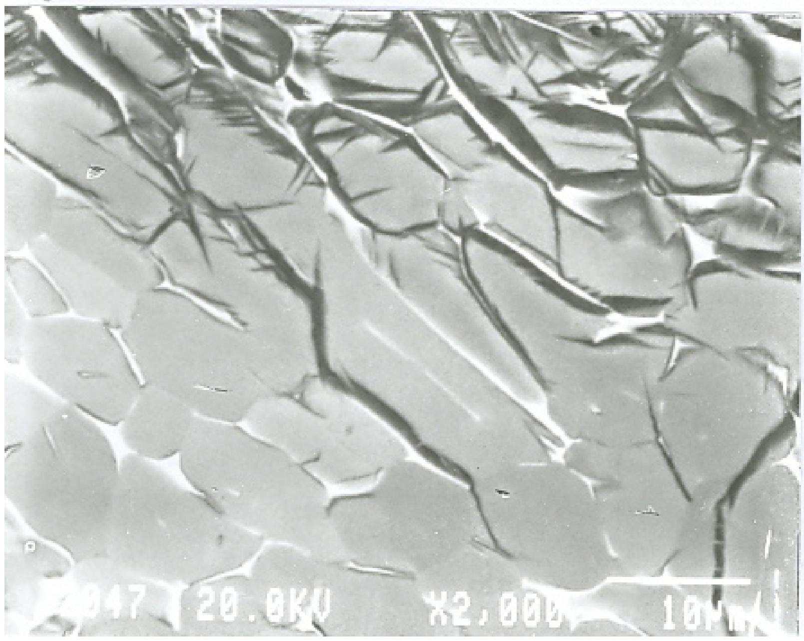

Figure 7. Back scattered electron image of Ti Gr-12 specimen tested at a strain rate of 2x10-7 s-1 in sea water with a cathodic polarization of -1500 mV (Ag/AgCl).

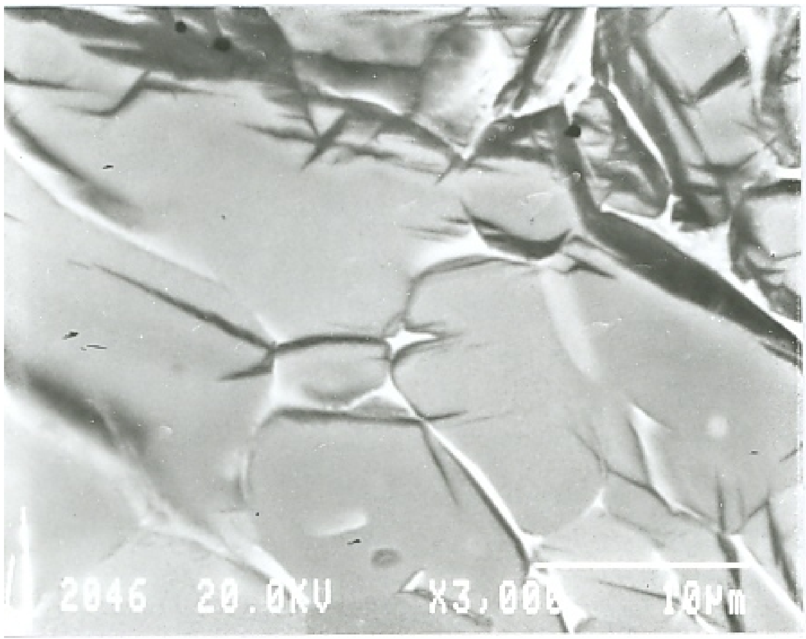

Figure 8. Back scattered electron image of Ti Gr-12 specimen tested at a strain rate of 2x10-7 s-1 in sea water with a cathodic polarization of -1500 mV (Ag/AgCl).

5.0 CONCLUSIONS

No sensitivity to Stress Corrosion Cracking was observed for titanium alloys grades 2, 5 and 12 when tested in sea water at temperatures up to 170ºC.

No sensitivity to Hydrogen Assisted Stress Cracking was observed for titanium alloys grades 2 and 5 when tested in sea water and with cathodic polarization of up to -1500 mv (Ag/AgCl).

However, Ti Gr-12 alloy has suffered loss of ductility and secondary cracking due to hydride precipitation when cathodic polarization is applied to the specimen during the SSR test, that showing a clear sensitivity to Hydrogen Assisted Stress Cracking.

The present work consists of an example of the hydrogen damage to materials by the hydride formation type.

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