HYDROGEN ASSISTED STRESS CRACKING OF TITANIUM ALLOYS

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ABSTRACT

The behaviour of Titanium Grades 2 and 12 alloys under hydrogen assisted stress cracking conditions has been studied by means of the slow strain rate technique. Tests have been performed in air and synthetic sea water and hydrogen was potentiostatically produced on the specimen surface during the test. Measurements of elongation, reduction of area, maximum load and true stress at fracture as well as metallographic and fractographic studies have been carried out in order to assess the loss of ductility of the studied alloys. Hydride penetration and cracking with a slight loss of ductility was observed for Ti Gr-12 when the highest cathodic potential was applied. The best behaviour against hydrogen assisted stress cracking was shown by Ti Gr-2 samples; although a thick hydride layer grew on the specimen surface and some lateral cracking appeared when -1500 mV (SCE) polarization was applied to the specimen no loss of ductility was observed.

KEYWORDS

Titanium, cracking, hydrogen, slow strain rate, embrittlement.

INTRODUCTION

Titanium and its alloys are increasingly being used in conditions where a high corrosion resistance is required. Moreover, its good mechanical properties/density ratio make these materials very attractive for applications in which reducing weight is an important consideration. Unalloyed titanium is successfully being used in marine and certain chemical industry equipments because of its excellent corrosion resistance due to the high stability, adherency and protective character of the titanium oxide. Titanium behaves satisfactorily as long as the media is oxidizing or slightly reducing, but if the reducing character of the environment increases, the titanium is galvanically coupled to some less noble material or some special situation where hydrogen can be formed on the material surface takes place, then there is a risk of hydriding and embrittlement.

EXPERIMENTAL

Hot rolled, cleanned and annealed 6 mm. thick Titanium Grades 2 and 12 plates were studied in the present work. Their chemical composition and mechanical properties are given in Tables 1 and 2.

Table 1. Chemical composition of materials tested (Weight %)

	Element							
Alloy	N	C	H	Fe	O	Mo	Ni	Ti
Ti Gr-2	0.0032	0.005	0.0030	0.048	0.126	-	-	Bal
Ti Gr-12	0.017	0.010	0.0021	0.11	0.15	0.26	0.66	Bal

Table 2. Mechanical properties of materials tested (transverse)

Alloy	Y.S. 0.2% (MPa)	U.T.S. (MPa)	E (%)
Ti Gr-2	430	499	31
Ti Gr-12	484	587	20

Metallographic samples were prepared and optically studied; their microstructure is shown in Fig. 1, where an equiaxed alpha microstructure can be observed for Ti Gr-2 and elongated alpha grains with intergranular transformed beta for Ti Gr-12.

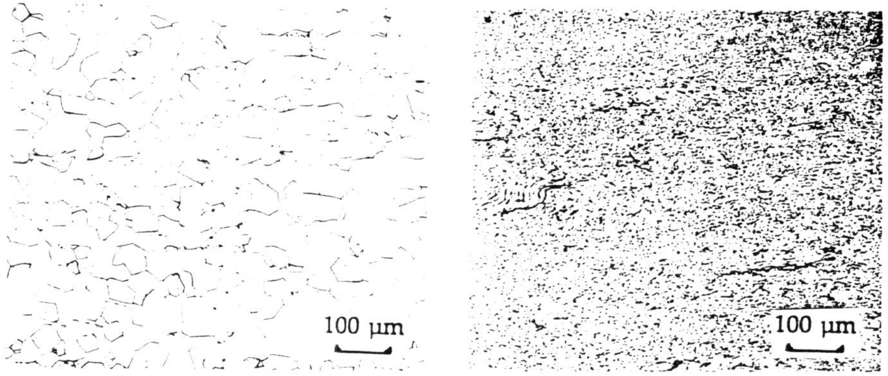

Fig. 1. Microstructure of: a) Ti Gr-2 (x100). b) Ti Gr-12 (x100).

Three mm diameter round tensile specimens in the transverse sense to the rolling direction were machined and finished with 600 grade emery paper. Slow strain rate tests in air and synthetic sea water were performed at room temperature in a K & H CERT 2000 electromechanical tensile testing machine. Hydrogen was cathodically produced on the specimen surface using a Wenking LT 78 potentiostat. The specimen was located in a metacrylate cell together with the reference (SCE) and counter (graphite) electrodes. Three different potentials were used: free potential, -1000 and -1500 mV (SCE). Strain rates used were 1.5 x 10^{-6}, 3 x 10^{-7} and 2.4 x 10^{-7} s^{-1} for Ti Gr-2 and 3 x 10^{-7} and 2 x 10^{-7} s^{-1} for Ti Gr-12.

Maximum load, elongation, true stress at fracture and reduction of area were the parameters measured to assess the loss of ductility. In order to quantify the hydriding of the alloys under different testing conditions, samples from the specimens' gauge lengths were analyzed using an automatic LECO RH1E hydrogen analyzer.

RESULTS

The results obtained in the SSRT tests are summarized in Figures 2 and 3 where Maximum Load, Elongation, True Stress at Fracture and Reduction of Area are plotted versus applied Polarization for each material and strain rate.

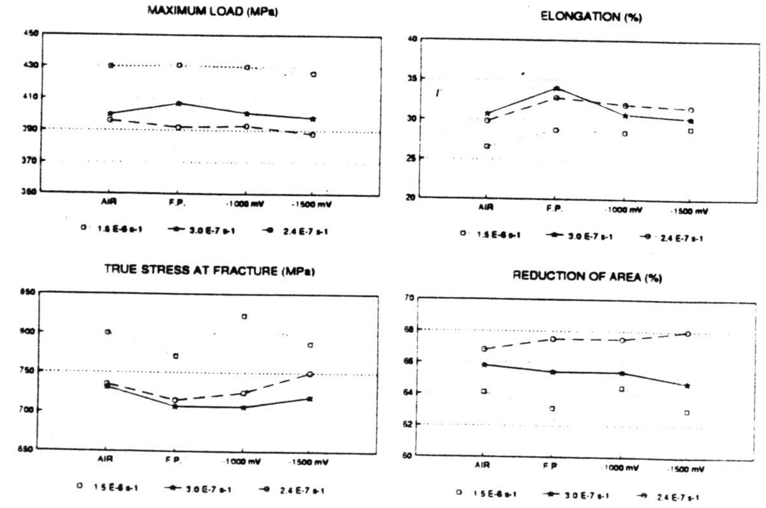

Fig. 2. Results of SSRT tests for Ti Gr-2.

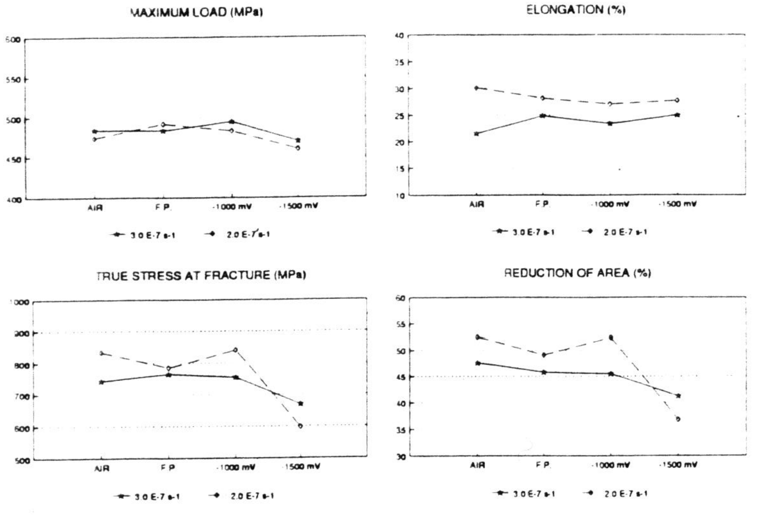

Fig. 3. Results of SSRT tests for Ti Gr-12.

Hydrogen analysis results are summarized in Table 3.

Table 3. Hydrogen Content (ppm) of tested speicmens.

Test Conditions	H (ppm) Ti Gr-2	H (ppm) Ti Gr-12
Air	20	23
-1000 mV	39	60
-1500 mV	232	320

Ti Gr-2 has shown no loss of ductility as a function of the cathodic potential for any of the strain rates used. (Fig. 2). Hydrogen analysis show that appreciable hydriding does not occur until the -1500 mV cathodic potential is applied to the specimen. This is in agreement with what is observed in the metallographic studies where no hydrides are detected until the highest cathodic polarization is used; in this case superficial hydriding and some lateral secondary cracks near the surface are present for all the strain rates used. Secondary cracking is more severe, as expected, in the specimen tested at the lower strain rate; some of this cracks can be observed in Fig.4.

Fig.4.- Optical micrograph showing lateral secondary cracks starting in the hydride layer in Ti Gr-2 tested at 2.4 x 10^{-7} s^{-1} strain rate with -1500 mV (SCE) cathodic polarization.

Specimens' fracture surfaces were studied by means of the scanning electron microscope. The fracture mode was ductile for all test conditions, even when the highest cathodic potential was applied to the specimen, the fracture surface was mainly ductile and only some short brittle areas have been observed in the starting of cracks.

Sensitivity to the hydrogen assisted stress cracking has been more evident for Ti Gr-12 since it has suffered some loss of ductility mainly manifested in the reduction of area and consequently in the true stress at fracture. (Fig.3). As in the case of Ti Gr-2, metallographic studies and hydrogen analysis show no important hydriding until the highest cathodic potential is applied to the specimen. Fig.5 shows an optical micrograph of a specimen tested at 2 x 10^{-7} s^{-1} strain rate.

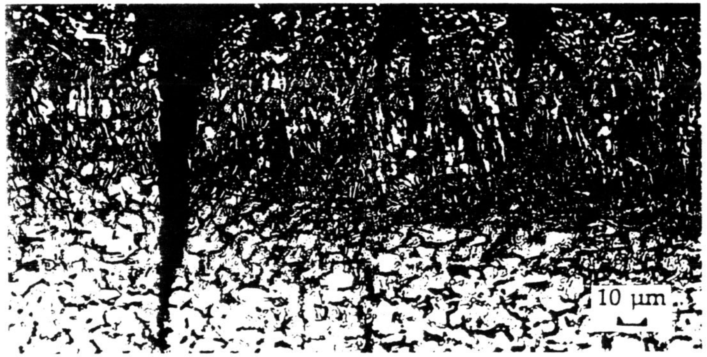

Fig.5.- Optical micrograph of the lateral surface of Ti Gr-12 tested at 2 x 10^{-7} s^{-1} strain rate with -1500 mV (SCE) cathodic polarization.

Considerable hydriding with important diffusión towards the bulk material and extensive secondary cracking along the gauge length of the specimens is seen. The fracture mode observed in scanning electron microscope studies is ductile for all testing conditions except when -1500 mV (SCE) polarization is used, case in which a more brittle like manner in the begining of main crack is detected.

DISCUSSION

The resistance of titanium grades 2 and 12 to stress corrosion cracking in synthetic sea water has turned out to be excellent since no secondary cracks, nor losses in ductility have been observed in tests performed with different strain rates at free potential. When cathodic polarization is used to produce hydrogen on the specimen surface during the test, the behaviour of the studied alloys has changed. In fact, it has been observed that hydrogen produced on the Ti Gr-2 specimen surface during the test forms a hydride layer of 40 m and also secondary cracks of up to 70 m. In Ti Gr-12 hydrogen has diffused into the material forming hydrides to a maximum depth of 120 m and secondary cracks of 200 m have been observed.

The different behaviour of these alloys seems to be associated with the different penetration capacity and solubility of hydrogen in each alloy, and can be explained taking into acount the following considerations.

The beta phase content is negligible for Ti Gr-2 and 3% in volume for Ti Gr-12.

The solubility of hydrogen in alpha (c.p.h.) titanium increases from 30-45 ppm at room temperature to 1500 ppm (6,72 at.%) at the eutectic (300ºC) according to results obtained by Vitt and Ono; at this temperature the solubility in the beta (b.c.c.) phase measured by San Martin and Manchester is 13200 ppm (39 at.%).

The diffusivity of hydrogen in alpha titanium is considerably lower than in the beta phase; Phillips et al. found that alpha titanium's diffusion coeficient over the temperature range 25 to 100ºC is given by:

$$D_\alpha = 6 \times 10^{-2} \times \exp(-14400 \pm 800/RT)\ \mathrm{cm}^2 \times \mathrm{s}^{-1}$$

Which yields a value of $3.2 \times 10^{-12}\ \mathrm{cm}^2 \times \mathrm{s}^{-1}$ at 25ºC, too low for any appreciable diffusion to be observed.

On the other hand, Holman et al. determined the diffusion coeficient in a beta titanium alloy over the temperature range 20 to 500ºC finding the expression:

$$D_\beta = 1.58 \times 10^{-3} \times \exp(-5140 \pm 300/RT)\ \mathrm{cm}^2 \times \mathrm{s}^{-1}$$

Giving a value of $3.3 \times 10^{-7}\ \mathrm{cm}^2 \times \mathrm{s}^{-1}$ at 25ºC, 10^5 times higher than in the alpha phase.

Therefore the superficial hydride layer formed on the Ti Gr-2 specimen can be explained by the low solubility and diffusivity of hydrogen in this completly alpha alloy. In the case of Ti Gr-12 the small amount of beta phase channels hydrogen towards the bulk material increasing its penetration; but when saturation of hydrogen is reached, hydrides precipitate in the alpha phase allong the grain boundary; this can be seen in Fig. 6 showing a backscattered electron image of a Ti Gr-12 specimen tested with the -1500 mV cathodic polarization.

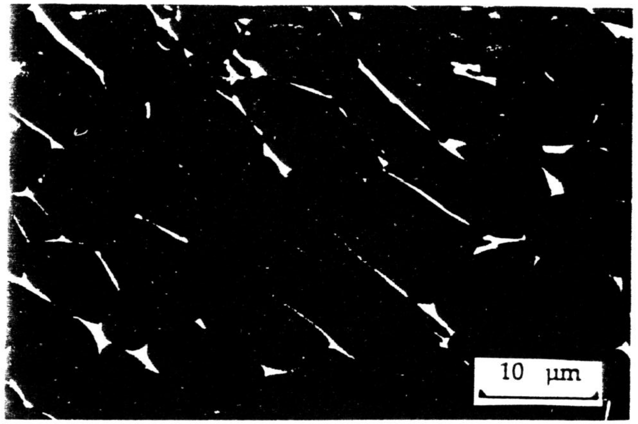

Fig.6.- Backscattered electron image of Ti Gr-12 specimen tested with -1500 mV (SCE) cathodic polarization.

Hydrides (dark) precipitate in the alpha phase (grey) allong the intergranular beta phase (bright). Then, the loss of ductility experimented by Ti Gr-12 is likely to be promoted by the formation of these hydrogen rich phases (hydrides) along the phase boundary.

CONCLUSIONS

- Hydriding of Titanium Grades 2 and 12 strained in sea water does not occur when cathodically polarized at potentials more positive than -1000 mV (SCE).
- Titanium Grade 12 suffers hydride cracking and some loss of ductility when slowly strained and polarized at -1500 mV (SCE).
- Titanium Grade 2 suffers superficial hydriding and some cracking but no loss of ductility has been observed when cathodically polarized at -1500 mV.
- Beta phase content seems to play a fundamental role in the hydriding and loss of ductility of titanium alloys while strained and cathodically polarized.

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