INVESTIGATION ABOUT THE STRESS CORROSION CRACKING OF TI-6AL-4V

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Abstract

Although the titanium alloys represent an optimal solution for several applications, they suffer from the detrimental effect related to the stress corrosion cracking (SCC) which can take place also in the most used Ti-6Al-4V. This study is focused on the characterization of the SCC on this alloy and it has been performed through the mechanical fracture tests realized within an environment of synthetic sea water featured by two levels of NaCl concentration. The identification of the Ti-6Al-4V behaviour in these situations is very significant because it can be often used for the substitution of more expensive alloys (i.e. cupronickel, monel etc.). The toughness tests realized in air and in the sea water solutions have been performed through the use of CT type specimens taken from a hot rolled plate. The fatigue crack propagation has been performed in air along the direction perpendicular to the rolling one (L-T specimens). The macroscopic analysis of the fracture phenomenon revealed the change of the propagation direction as a function of the NaCl concentration and the applied deformation rate. The unstable crack becomes parallel to the rolling direction as the deformation rate lowers and as the NaCl concentration increases. The same environmental and chemical condition produces a significant decrease of the K_{ISCC} value. The SEM-EBSD observation has pointed out a clear dependence of the crack propagation pattern on the crystallographic orientations induced in the alloy by the former plastic deformation process.

Riassunto

Sebbene le leghe di titanio rappresentino una soluzione ottimale per molte applicazioni, esse possono essere soggette alla corrosione sotto sforzo (SCC). Questo studio è focalizzato sulla caratterizzazione della SCC per la lega Ti-6Al-4V mediante test di meccanica della frattura realizzate in un ambiente di acqua di mare sintetica caratterizzata da due livelli di concentrazione di NaCl. L'identificazione del comportamento della lega Ti-6Al-4V in questa situazione è molto importante perché essa può essere utilizzata per sostituire materiali più costosi (cupronikel, monel, ecc). Le prove di tenacità, realizzate sia in aria che in acqua di mare sintetica, sono state eseguite su provini CT prelevati da una lamiera laminata a caldo. La cricca di fatica è stata fatta propagare in aria lungo la direzione perpendicolare a quella di laminazione (campione L-T). Le analisi macroscopiche della frattura rivelano il cambiamento della direzione di propagazione in funzione della concentrazione di NaCl e dalla velocità di deformazione applicata. La propagazione instabile diventa parallela alla direzione di laminazione al diminuire della velocità di deformazione e all'aumentare della concentrazione di NaCl. Le stesse condizioni ambientali e chimiche producono un significativo decremento del valore di $K\text{-}_{ISCC}$. Le osservazioni condotte mediante SEM-EBSD hanno mostrato una chiara dipendenza della propagazione della cricca dalla orientazione cristallografica indotta nella lega del precedente processo di deformazione plastica.

INTRODUCTION

In the last decades the use of the titanium alloys has known a significant increase also within corrosive environment, in which the passivation properties of the titanium alloys can be fully exploited. This feature associated with the high strength vs. density ratio and the thermal stability makes the titanium alloys a strategic material in some critical applications related to the mechanical, aeronautical and aerospace fields. [1,2,3,4,5,6,7].

The pure titanium undergoes an allotropic transformation at 882°C and above this temperature shows a bcc lattice (β phase), while at a lower one it is featured by a hcp lattice (α phase). The α phase of titanium is characterized by a c/a ratio (1.587) lower than the one featuring magnesium and zinc. This implies a greater number of basal planes per unit volume which are the most favourable to grant the plastic deformation in hcp lattice. The mechanical properties of titanium are greatly influenced by the solution of little quantity of gas content which can cause a wide variability of the mechanical properties. It is probable that the contents of the gaseous species can compromise also the SCC performances of titanium alloys, in which the crack instable propagation can generally be promoted by the anodic dissolution of the crack tip or by the hydrogen solution within the alloy.

On the other hand, the pure titanium does not suffer the SCC phenomenon neither in hot saline solution or in sea water, while its alloys can undergo it. The problem related to the possibility of SCC in titanium α-β alloy in sea water environment is one of the most interesting aspects implied in the designing of structures built to operate within aggressive environment. The oxide passivation layer of the titanium alloys is resistant in humid atmosphere and in presence of nitric acid, but it is subject to a significant corrosion rate in all the acid environments producing hydrogen in their interaction with the metal [8,9]. In this study, the sensibility of the largely most applied α-β alloy Ti-6Al-4V (grade 5) [4,10,11,12] has been studied in synthetic sea water through mechanical fracture tests.

The SCC phenomena is developed through the crack nucleation and its successive propagation under the cooperating action of the applied stress and of the corrosion process [4,13]. Within the nucleated cracks a variation of the concentration of the aggressive agents takes place and this leads to a stable propagation of the cracks with a speed included in the range of 10^{-2}-10^{-7} mm/s. The experience developed in this field [13,14] has permitted to underline some qualitative rules of general validity which can help in the designing of the experimental activity to investigate the SCC phenomenon:

- the SCC takes place under tensile stress and not under compression, because the first ones open the surface of the cracks and so promote their contact with the aggressive solution contained in the environment;
- the stress corrosion interests the alloys which can produce a passivation layer;
- some alloying elements decrease the possibility of the development of the SCC (i.e. palladium in titanium alloys);
- the permanence of the titanium alloys in the thermal range between 500°C and 800°C can largely improve the possibility of SCC.

The instable propagation of the cracks can occur only if the stress intensification factor is greater than the critical value K_{ISCC}, which is defined for a particular environment as:

$$K_{ISCC} = A\sigma\sqrt{\pi a} \tag{1}$$

where *A* is the shape factor of the crack, ς is the average applied stress on the resistant area, *a* is the crack length. The propagation of the crack as a function K_I agrees always with a typical trend (Figure 1). The SCC can take place only in particular zones on the potential-current density characteristic curve of the anode featured by a active-passive behaviour (Figure 2).

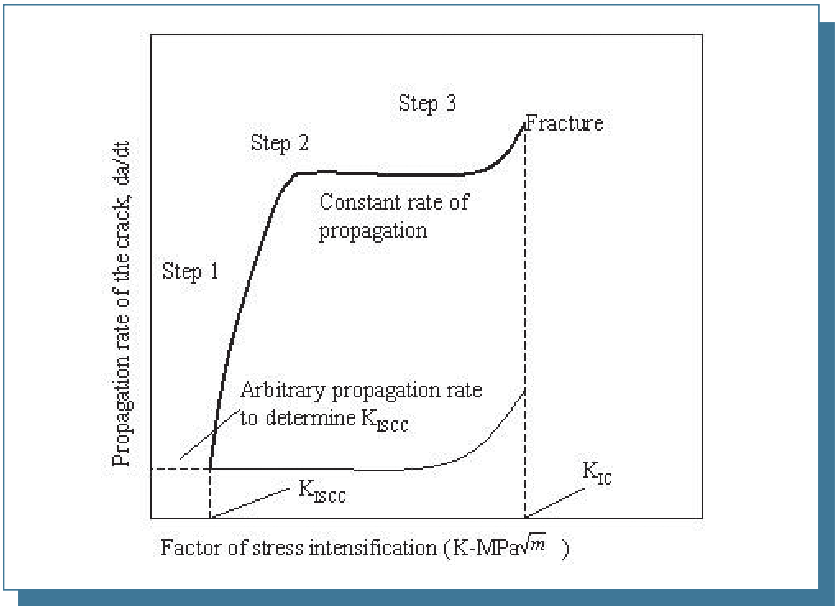

Fig. 1: Propagation rate of the crack as a function of K_{IC} in a corrosive environment and without it.

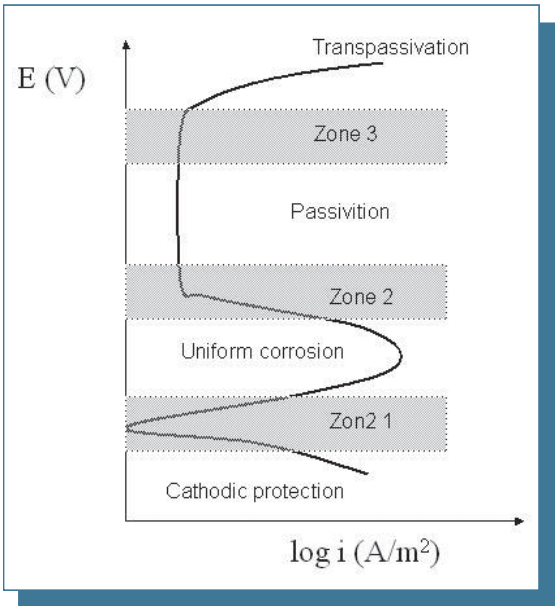

Fig. 2: The grey zones represent the situations in which the SCC phenomenon can start up.

The main aim of the present investigation is a measurement of the toughness decreasing revealed on hot rolled Ti-6Al-4V as function of the variations in two main factors of influence such as concentration of chlorides and imposed deformation rate, which are involved in the SCC phenomenon. Moreover, the performed toughness tests can cast a new light on the relation between the crystallographic orientations and the development of SCC in Ti-6Al-4V.

Table 1. Chemical composition of the tested Ti-6Al-4V.

Elements	N	C	H	Fe	O	Al	V
%wt	0.009	0.007	0.0007	0.11	0,162	6.25	4.05

Table 2. Fundamental mechanical properties measured on the tested Ti-6Al-4V.

Property	Value
Rm (20°C)	999 MPa
Rs (20°C)	961 MPa
HV	352

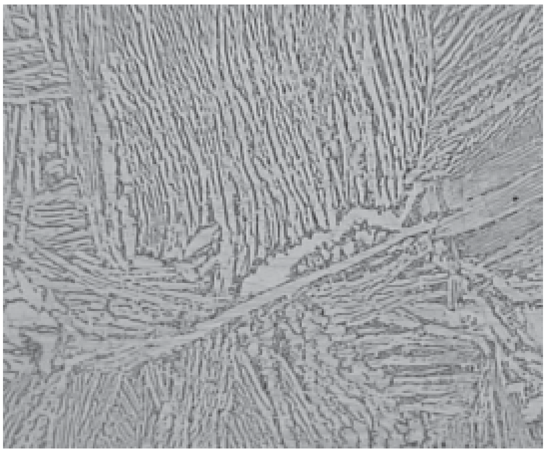

Fig. 3: Microstructure of the studied Ti-6Al-4V revealed after Kroll etching (200x).

EXPERIMENTAL PROCEDURE

The tested α-β alloy is a typical Ti-6Al-4V (grade 5) featured by a chemical composition (Table 1) in agreement with ASTM B-265-95 and the mechanical properties measured by tensile test performed on specimens taken from a direction parallel to the rolling one and through Vickers microhardness test are within the range required for this material (Table 2) [12]. The microstructure observed after the application of Kroll etching (1 ml HF, 3 ml HNO_3, 96 ml H_2O) has revealed a classical microstructure of the hot rolled α-β titanium alloys (Figure 3). The CT specimens have been sampled from a hot rolled plate (300x400x16mm).

The precracked samples have been prepared on the basis of standards ASTM E-1823-96, E-399-90 and E-1290-90, which provide the indications about the size and the proportions of the tested specimens (Figure 4a). All the used specimens have a geometrical shape featured by 37.5x36x15mm and they have been produced with the pre-crack perpendicular to the rolling direction (L-T direction) (Figure 4b). Three extensimeters have been pasted on the specimen surfaces to measure the deformation rate of the stressed specimens in the regions adjacent to the crack tip during the final tensile tests. They have been also insulated by the application of an electrical insulating epoxy glue.

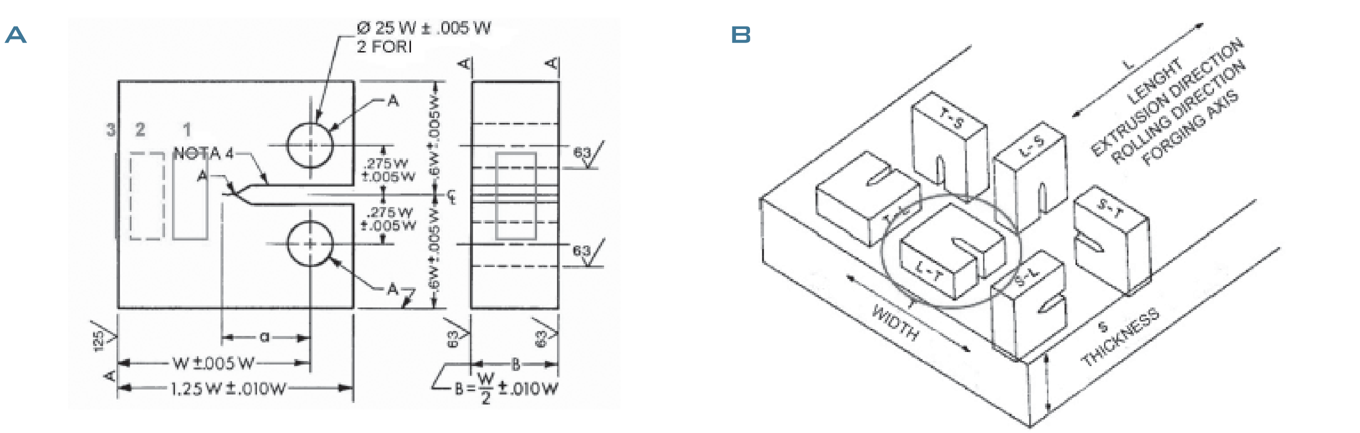

Fig. 4: (a) Proportions of the specimens according to ASTM E399-90 and position of the applied extensimeter; (b) crack plane orientation.

The pre-crack has been propagated through the application of a pulsing fatigue cycle (Table 3). The growth of the fatigue crack has been monitored through an optical microscope and its length reached an average value of 5.1mm.
The high number of the factors of influence which can determine the start up of the SCC and the determination of the sensibility of a particular alloy to this phenomenon of failure can be difficult, so the attention has been focused on two different parameters: chloride content of the synthetic sea water and the imposed deformation rate.

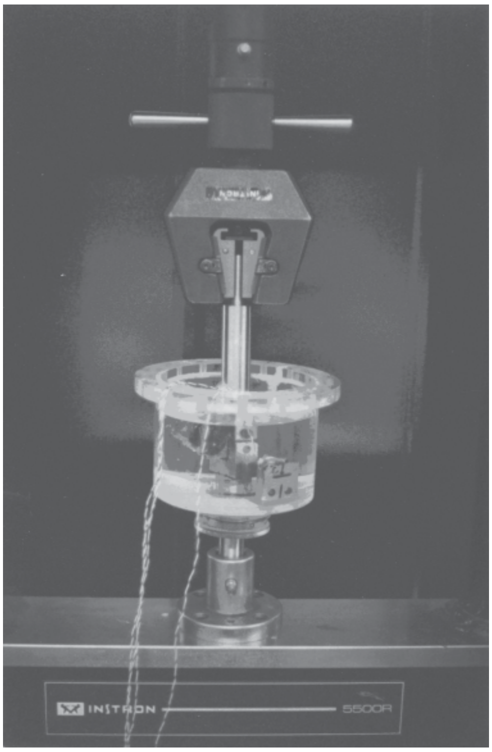

Fig. 5: Device applied to the tensile test machine to develop the thoughness tests on CT specimens within an environment of synthetic sea water.

TABLE 3. PARAMETERS USED FOR THE PULSING FATIGUE PROPAGATION OF THE PRECRACK.

Parameters of the precracking fatigue cycle	
Frequence [Hz]	25
Maximum applied stress [kN]	18 (50% R_{sn})
Temperature [°C]	20

The synthetic sea water has been formed according to ASTM D-1141 with two different NaCl contents (2% and 3.5%). It is worth noting that there are many differences between the real sea water and the synthetic one as the absence of biological species, thermal variations, stirring of the fluid flow etc..
In order to realize SCC tests in sea water solution, the tensile test machine has been equipped by a special device (Figure 5) which allows the complete immersion of the specimens in the corrosive liquid phase. The steel clamps connecting the specimens with the tensile machine have been covered by a polyethilene film to avoid the formation of an anodic-cathodic coupling between the specimens and the test equipment.
The specimens which underwent the fracture mechanic test have been observed through SEM-EBSD (Scanning Electron Microscope equipped by Electron Back Scattering Diffraction) to measure the orientations of the crystal lattices belonging to α phase and β phase.
The electrochemical potential of Ti-6Al-4V has been continuously measured during the test and it has assumed an average value of 0.08V with a standard deviation that is 3% of the average value. The well known equation (2) has allowed the computation of the K_{IC} and K_{ISCC} for the studied alloy in different conditions:

$$K_{IC} = \frac{P_Q}{BW^{0,5}} f(a/W) \qquad (2)$$

where *B* and *W* are the characteristic geometrical dimensions of the specimen (Figure 4). The value f(a/W) (shape factor) and the load P_Q [N] have been determined according to the indications contained in ASTM E-399.
The final tensile test on the pre-cracked specimens have been performed through four different strain rates: 0.02mm/min, 0.015mm/min, 0.01mm/min, 0.005mm/min and for each condition three different environments have been applied: air, synthetic sea water featured by 2%NaCl and synthetic sea water featured by 3.5%NaCl. Three specimens have been tested for each condition.
The fractographic analysis has been realized through the use of optical and SEM microscopy.

RISULTS AND DISCUSSION

The first interesting result is related to the macroscopic development of the cracks (Figure 6). In the represented example it is possible to reach a first statement about the propagation direction as a function of the applied environment:

- the direction of the crack growth developed in air is perpendicular to the loading one (Figure 6a);
- the direction of the crack growth developed in 3.5% NaCl follows a direction parallel to the loading one (Figure 6c);
- the direction of the crack growth developed in 2% NaCl shows an intermediate pattern between the former two ones (Figure 6b).

On the basis of the experimental data obtained through the tensile test of the CT specimens and through equation (2), the average values of K_{IC} have been computed for the different conditions (Table 4). The values obtained in air are consistent with the results that can be found in literature for the studied material [12,15,16]. In the fracture process, the role covered by the environment appears to be very significant as the deformation rate assumes

TABLE 4. AVERAGE VALUE OF THE MEASURED K_{IC} ($MPa\ m^{0.5}$) AND THE RELATED STANDARD DEVIATION IN THE DIFFERENT TEST CONDITIONS (THE VALUES IN THE ROUND BRACKET ARE THE STANDARD DEVIATIONS).

Displacement	Air	NaCl 2%	NaCl 3.5%
0.02 mm/min	73 (2)	72 (2)	72 (2)
0.015 mm/min	74 (2)	68 (2)	62 (2)
0.01 mm/min	73 (3)	64 (2)	58 (2)
0.005 mm/min	74 (3)	60 (2)	53 (3)

the lowest values. A general trend can be clearly underlined: the toughness of the Ti-6Al-4V becomes progressively lower as the deformation rate decreases and the chloride concentration increases. At 0.02mm/min the K_{IC} values appear to be nearly constant, probably because in this condition the rate of the load application is so fast that the diffusion of the chemical species inducing the brittleness cannot develop to the level which produces the decreasing of the material thoughness.
The analysis performed by optical microscope have pointed out that the crack interesting the fracture specimens propagate through a transgranular pattern and the intergranular modality is present only in little regions (Figure 7). The fractographic analysis performed through SEM on the fatigue precracked zone has allowed to identify the presence of dimples in the fracture surface and the secondary fractures starting from the surface itself. These regions can be classified as interested by a ductile micromechanism of fracture (Figure 8).
In the region interested by a process of unstable crack propagation the morphological aspect of the fracture depends on the environmental conditions and on the applied deformation rate. The SEM observations allow to state that the increasing of the chloride concentration and the decreasing of the deformation rate imply a progressively wider area of the plane facet featuring the brittle micromechanism of fracture. The facets associated to the brittle micromechanism are separated by wriklings which become deeper as the chloride concentration increases and the strain rate decreases (Figure 9, Figure 10). The microscopic fractography confirms the toughness trend associated to the variation of the modified factors of influence.
The SEM-EBSD investigations have permitted to define the textures of the phases contained in the alloy [17] (Figure 11, Figure 12) and their relation with the evolution of the SSC. Actually, the sharp variation of the path followed by the crack during its macroscopic development in the aggressive environment seems to suggest that the statistical crystallographic orientation of the lattices can play a very significant role in ruling the direction of the crack propagation.
The brass {011}<211> and the copper {112}<111> components of the textures have been observed in bcc phases and so the <111> and <211> directions seem to be parallel to the path followed by the crack during its propagation when the loading condition and the environment promote the significant decreasing of the measured toughness. On the other hand, in the case of the hcp α phase of the lattice the direction parallel to the rolling

Fig. 6: Examples of the macroscopic aspect of the development of the cracks produced at a deformation rate of 0.015 mm/min, (a) in air, (b) synthectic sea water-2% NaCl, (c) synthetic sea water-3.5% NaCl.

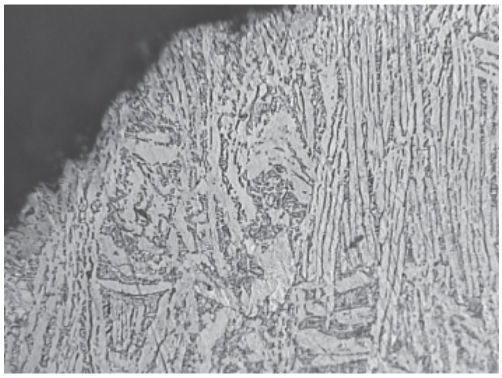

Fig. 7: Example of a zone interested by the fracture process (200x).

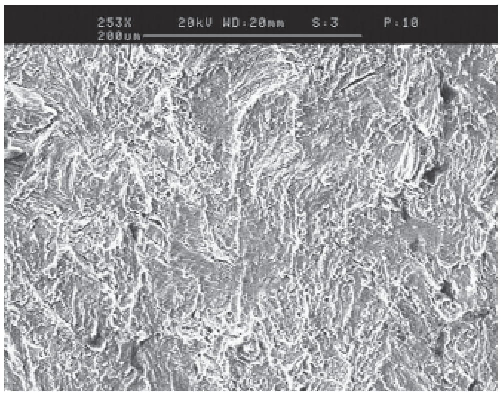

Fig. 8: SEM image of the precracked region (250X).

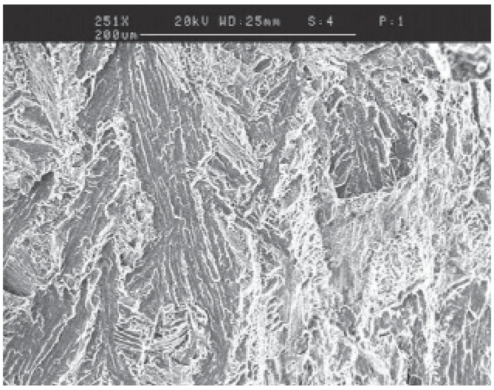

Fig. 9: Characteristic aspect of the fracture surface in synthetic sea water-2% NaCl deformed at a strain rate of 0.015mm/min (250X).

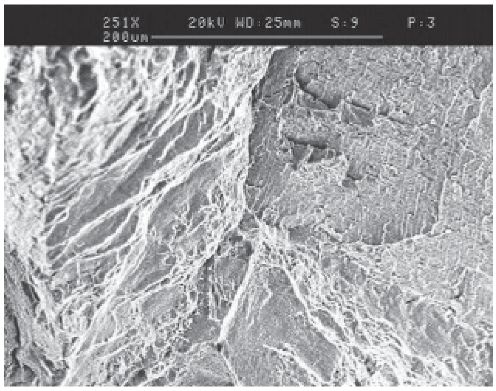

Fig. 10: Characteristic aspect of the fracture surface in synthetic sea water-3.5% NaCl deformed at a strain rate of 0.015mm/min (250X).

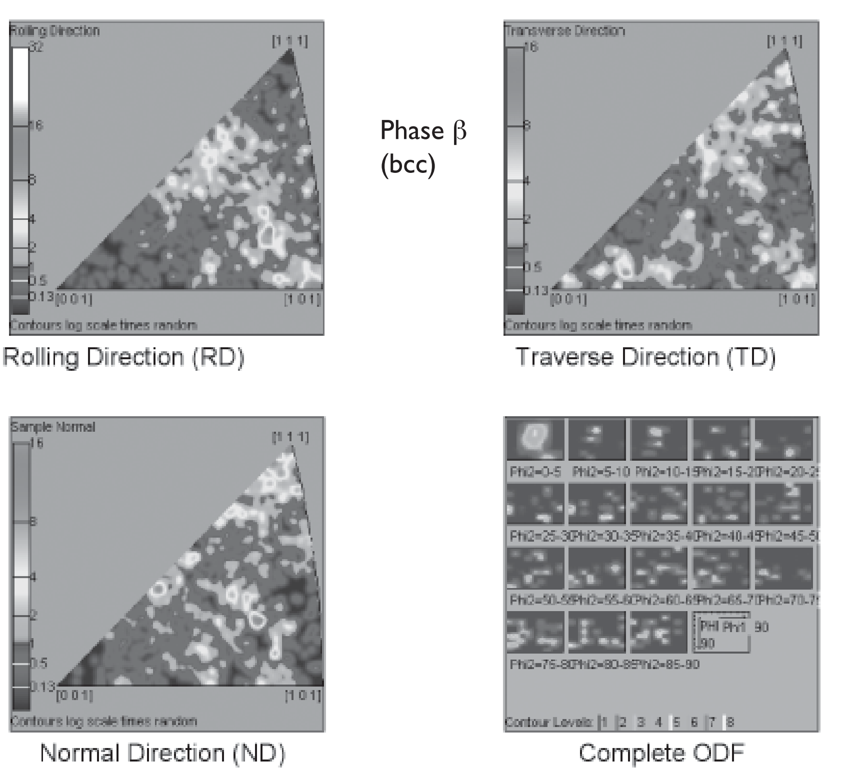

Fig. 11: Inverse polar figure of the β phase.

one are the ones in the proximity $<1\bar{1}00>$. This direction of the lattice coincides with the direction of the side of the hexagon defining the basal planes. There is a very interesting difference with the development of the crack observed in air which seems to interest the directions near $<1\bar{1}00>$ in β phase and the ones near $<2\bar{1}\bar{1}0>$ direction in the α phase. However, the textures featuring the α phase are sharper and in a hcp cell the $<1\bar{1}00>$ directions on the intermediate plane between the upper and the lower basal planes can be a favourable zone for the hydrogen accumulation and this phenomenon can damage the structural integrity of the lattice. Although the precise measurements of the solute hydrogen are not available, the hypothesis about the damaging role developed by hydrogen seems to be corroborated by the significant toughness decrease associated to the slowest strain rates. The slowest strain rates can leave to the hydrogen a longer time for its diffusion within the stressed lattices and so to develop its damaging effect. In this condition the observed misorientation concentrated

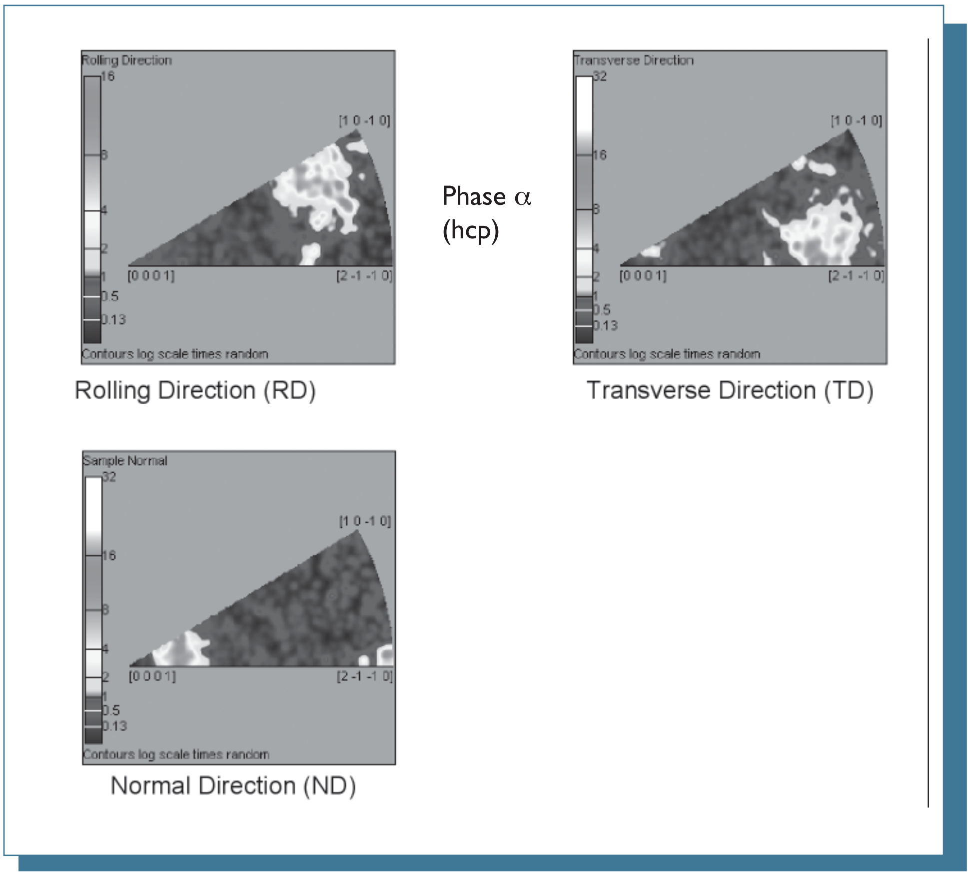

Fig. 12: Inverse polar figure of the α phase.

around the lower values of the relative angles among adjacent grains can be another critical factor, because the cracks advancing in a lattice damaged by the hydrogen along some specific directions cannot find a great obstacle on the grain boundaries (Figure 13) [18]. This evidence seems to suggest also a reliable explanation of the difficulty in observing the occurrence of SCC phenomenon on titanium alloys out of the laboratory equipment. Actually, the extremely slow strain rates (10^{-6}-$10^{-7}s^{-1}$) could be difficult to be met in industrial applications.

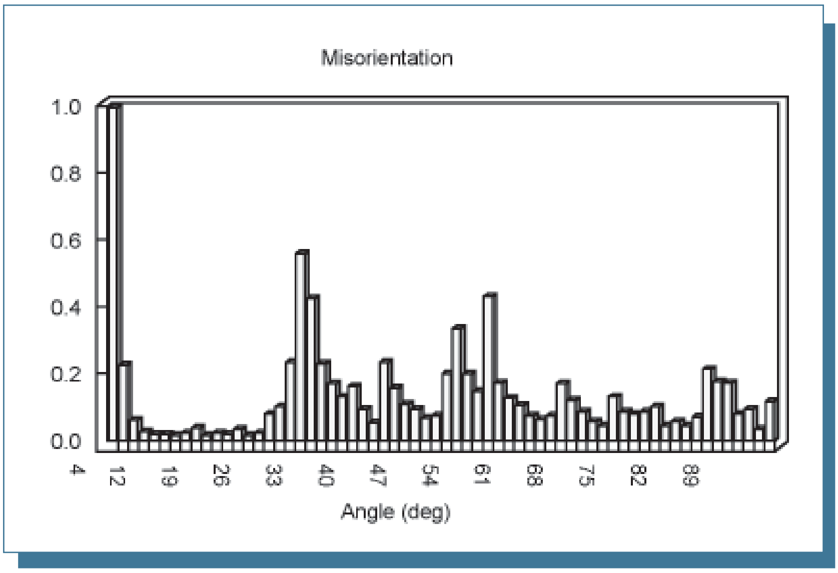

Fig. 13: Misorientation distribution of grains of the a phase within the observed titanium alloy.

CONCLUSIONS

The experimental results have pointed out that:

- Ti-6Al-4V suffers the SCC phenomenon in the synthetic sea water environment;
- the decrease of toughness is promoted by high chloride concentration and by the very slow strain rates;
- the strain rate needed to activate the SCC within the synthetic sea water can be stated in the order of 10^{-6}-10^{-7} s^{-1} and this can be the reason of the difficulty to observe the start up of SCC in the real situations out of the laboratory;
- the need of slow strain rate to observe the significant decrease of SCC suggests that the most probable responsible for the activation of the failure phenomenon is the damaging action of hydrogen which needs time to diffuse in the strained lattices;
- the fracture phenomena related to the SCC is concentrated along particular directions of the lattices, especially the ones near $<1\bar{1}00>$ directions of the α phase which, after the hot rolling, are mainly aligned with the rolling direction due to the formation of strong {0001}<100> components;
- in the cell of hcp lattice the <100> directions on the plane intermediate between the two basal ones is one of the most favourable regions in which the hydrogen can diffuse and accumulate to perform its damaging effect.

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