DISCONTINUOUS STRESS CORROSION CRACKING BEHAVIOR
OF Ti-6Al-4V IN SYNTHETIC SEA WATER WITH TEMPERATURE

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Introduction

Stress corrosion crack growth in titanium alloys is an activated process that has been investigated by several authors. The activation energies related to the stage II of the crack propagation are in a range of 13 to 21 KJ/mole (1-3). Our work on Ti-6Al-4V alloy in chloride aqueous solutions has shown that the variation of the crack growth rate with temperature is more complicated and a single law as \( \frac{da}{dt} = k \exp \left( \frac{-Q}{RT} \right) \) cannot describe entirely the observed phenomenon (4). In particular, a supplementary variation, which appears only in a narrow range of temperature is added to the variation of the crack growth rate corresponding to the activated process. Such a variation has not been found by other authors because it is a very sharp phenomenon occurring in a very narrow temperature range which only extremities are generally investigated. The first part of this paper is devoted to the influence of the specimen's crack orientation on this phenomenon.

Many investigators have observed that fracture topographies produced during stress corrosion cracking of titanium alloys exhibit fluted features intimately associated with cleavage of the alpha phase. Flutes appear also during subcritical cracking of zirconium alloys and it has been shown by Cox et al. (5-6) that these features are the result of a particular kind of slip deformation. Their experiments have shown that the flutes are non-complementary features, i.e. they are mirror image of one another on mating halves of the fracture surface. Moreover, the flutes are oriented at high angles to genuine cleavage features, and thus probably near to the prism planes. This observation has been confirmed by Wanhill (7) who found the flutes observed during stress corrosion cracking and liquid mercury embrittlement of a titanium alloy represent slip deformation surfaces composed of intersecting \{10\overline{1}0\} planes, and the author proposed a model to account for their formation. Therefore, it appears the material texture and consequently the specimen's crack orientation has to influence greatly the fractographic aspect, which is the purpose of the second part of this paper.

Experimental

The material used in this investigation is a commercial Ti-6Al-4V alloy supplied by Krupp, of the following nominal composition (Table 1):

**Table 1 - Chemical composition**

<table>
<thead>
<tr>
<th>Element</th>
<th>Al</th>
<th>V</th>
<th>Fe</th>
<th>C</th>
<th>H₂</th>
<th>O₂</th>
<th>N₂</th>
<th>Ti</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt %</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td></td>
<td>6.0</td>
<td>4.0</td>
<td>0.10</td>
<td>0.01</td>
<td>0.003</td>
<td>0.15</td>
<td>0.03</td>
<td>bal.</td>
</tr>
</tbody>
</table>
The as received 20 mm plate (annealed 1 hour at 650 °C, air cooled) is cut into two precracked specimen configurations: 10 mm thick cantilever specimen and 8 mm thick compact tension specimen (CT). The different crack orientations tested are shown on figure 1.

The tests are conducted in aerated substitute sea water (8) (pH 8 - 8.5) in a 0 - 85 °C temperature range. The load applied to the specimen is progressively increased until reaching or slightly exceeding the value of the stress intensity required to propagate a stress corrosion crack (KISCC). The propagation of the crack is then followed up to the fracture with binocular lens. The measurement of the crack length at regular time intervals (5 or 15 s. depending on the crack growth rate) gives the value of the crack growth rate.

Results and discussion

1. Crack growth kinetics.

For titanium alloys the variation of the crack growth rate with the stress intensity $K_I$ generally presents two different stages. According to the usual statements for aqueous media close to neutrality, the stage I (where $da/dt$ is strongly dependent on stress intensity $K_I$) is not observed in this work; only the stage II (crack growth rate independent of stress intensity) is well defined.

The experimental results allow the determination of the influence of the temperature on crack growth rate (figures 2-3). The curves are drawn using the least square method; the error margin for the calculated apparent activation energy is determined for 95 % confident limits.

![Figure 1 - Different crack orientations of tested specimens.](image1)

![Figure 2 - Temperature effect on crack growth rate for WT specimens.](image2)
The variation of crack velocity with temperature for WT crack orientation cantilever specimens is following the general equation:

$$\frac{da}{dt} = k_1 \exp\left(-\frac{Q_1}{RT}\right)$$

with $$Q_1 = 15.0 \pm 5.8 \text{ KJ/mole}$$ (figure 2 - curve a)

From a larger number of tests, carried out with WT crack orientation compact tension specimens, it appears that the kinetic is more complicated, a discontinuity occurring at 37°C. Above this temperature, the variation of crack growth rate is similar to that observed for cantilever specimens:

$$\frac{da}{dt} = k_2 \exp\left(-\frac{Q_2}{RT}\right)$$

with $$Q_2 = 10.9 \pm 1.8 \text{ KJ/mole}$$ (figure 2 - curve b)

Below 37°C, the variation of crack growth rate is more important. For each temperature, the difference between the observed rate and the rate corresponding to the second equation can be represented by the equation:

$$\frac{da}{dt} = k_3 \exp\left(-\frac{Q_3}{RT}\right)$$

with $$Q_3 = 87.8 \pm 29.3 \text{ KJ/mole}$$ (figure 2 - curve c)

Therefore, the experimental points are situated near to the curve drawn from the equation:

$$\frac{da}{dt} = k_2 \exp\left(-\frac{Q_2}{RT}\right) + k_3 \exp\left(-\frac{Q_3}{RT}\right)$$ (figure 2 - curve d)

This phenomenon has not been observed with cantilever specimens because, owing to the little number of tests, no determination of crack growth rate has been made in the temperature range where the added variation of rate is clearly apparent.

With CT specimens which crack propagates in the rolling direction (WR and TR) the crack growth rates are more important. The general shape of the curves is also representative of activated processes with apparent activation energies equal to 17.7 ± 7.8 KJ/mole and 18.5 ± 3.0 KJ/mole for TR orientation and WR orientation respectively (figure 3).

Figure 3 - Influence of crack orientation on crack growth rate versus temperature curves: (1) and (2): WT, (3): TR, (4): WR.
For TR specimens, a discontinuity appears again, but at 27°C and with a minimum of the propagation rate. For WR specimens, we find a maximum as for WT specimens, but, owing to the little number of tests, its shape and position have not been accurately determined.

For WT specimens, the observed crack growth rates slower than for WR et TR specimens are related to the texture and the fibrous structure of the material (figure 4). These texture and fibrous structure are also responsible for RT and RW specimens (where the crack plane is perpendicular to the rolling direction), for cracks which lead to propagate in planes parallel to the rolling direction and so the crack growth rates could not be determined.

The presence of discontinuities on da/dt = f(T) curves may be correlated to the precipitation of a brittle titanium hydride phase which is often considered responsible for stress corrosion cracking of titanium alloys. Effectively, the titanium hydride TiH₂ undergoes a second order transformation (tetragonal γ → cubic γ) which involves a discontinuity in the variation of its lattice parameters with temperature. This transformation has been found by Yakel (9) on titanium hydride powder at 37°C, whereas other authors found it at about 25°C (10) (figure 5). These temperatures are near to the ones corresponding to the discontinuities observed for propagation rates, which justify the hypothesis that the two phenomena are related and thus that the hydride precipitation influences the propagation rate. Moreover, this influence may be different for the various crack plane orientations in relation to the hydride precipitation.

Figure 4 - Microstructure of the Ti-6Al-4V alloy (x 100).

Figure 5 - Variation of lattice parameters with temperature of titanium dihydride. The Yakel's curves concern titanium dideuteride.
plane which may explain the various curve shapes obtained. In the present state of our study these hypothesis have not been verified.

2. Fractographic aspect

According to other authors observations, the Ti-6Al-4V alloy stress corrosion fracture surfaces observed are composed of cleavage and fluted areas (figure 6). We can notice on these fractographs the complementary nature of cleavage and the noncomplementary nature of fluted features, the figures 6a and 6b corresponding to the two parts of a WT crack orientation specimen. This noncomplementary nature of flutes is more obvious on figure 7 where such features incompletely parted are seen in profile. Moreover, this fractograph shows the flutes oriented at high angles to cleavage features.

![Figure 6 - Mating halves of a WT specimen fracture surface (x 1000).](image)

Depending on the rupture cause, the alpha phase cleavage occurs along different kinds of planes. For stress corrosion cracking in chloride media, cleavage takes place on planes with high indices, 15° from basal plane, namely \{1017\} or \{1018\} (11). In the tested alloy the alpha phase basal plane is near to the RT plane of the plate. For WT and WR specimens, the crack propagation plane is consequently near to cleavage planes which leads to the observation of large cleavage areas. Moreover, these cleavage areas are not exactly plane surfaces, but they are composed of facets separated by small steps which allow to partly compensate for the slight difference of orientation between the cleavage planes and the crack propagation plane. These steps seem to occur along the beta phase as suggested in figure 8. This fractograph concerns a WR specimen which part of the fracture surface has been polished and chemically etched to examine the relation between the material structure and the fractographic aspect. This examination shows a very good coincidence, firstly between the beta phase orientation and the cleavage steps orientation and, secondly between the spacing of the aligned beta phase and the facets width.
For TR specimens where crack plane is at high angle from the alpha phase basal plane, the cleavage areas, approximately normal to the fracture surface, then appear smaller. Besides, the specimen orientation is favourable to the formation of flutes which are effectively numerous. So a waterfall like aspect may be found as on figure 9.

The less favourable orientation for cleavage and flutes formation for RT and RW specimens gives a less marked aspect. In particular, ductile fracture areas appear among finely mixed cleavage and fluted areas (figure 10).
STRESS CORROSION CRACKING OF Ti-6Al-4V

The temperature does not seem to have a great influence on fractographic aspect, and more especially no difference has been observed for specimens cracked on each side of the temperatures corresponding to discontinuities. However, for WT specimens, the flutes number is larger when temperature is lower.

It is also observed that frequently flutes are associated with secondary cracks. It may be assumed that flutes allow some joining of two cleavage planes occurring into two alpha grains. The probability for joining at extremities of cleavage surfaces is low. The case presented on figure 11 where the flutes intersect a cleavage plane inside the cleavage area is more probable. Fractographic examination of part A of the specimen then shows a secondary crack at the boundary between the cleavage plane and the fluted surface in grain b whereas it does not appear in part B. This assumption agrees with the observation, during the experiments, of small cracks sometimes appearing ahead the main crack till joining it afterwards. When the joining of two cleavage planes is not possible by a single flutes system, two flutes systems which meet together at a grain boundary may appear as schematized in figure 12 and illustrated in figure 6.

![Figure 11 - A flutes system joining cleavage planes.](image1)

![Figure 12 - Two flutes systems joining cleavage planes.](image2)

Our observations do not entirely agree with the model proposed by Wanhill (7). Effectively this model involves an entire flutes system occurring in a same alpha grain. However, in our case the size of flutes systems is larger than the alpha grain size. But, the Wanhill's model may be compatible if it is supposed that flutes occur in several alpha grains originated from a same previous beta grain and having a same crystallographic orientation. Our model also is only valid with this condition.

The Wanhill's model describes the flutes branched ends as being the consequence of a grain boundary proximity. But, as shown in figure 6, these branched ends appear inside the grain at the intersection with a cleavage facet and are absent near to the grain boundary which does not agree with the Wanhill's model.
Conclusion

It was shown that the stress corrosion crack growth kinetic of a Ti-6Al-4V alloy in chloride media in a 0-85 °C temperature range is not a single activated process: in the crack growth rate versus temperature curves, discontinuities were observed which may be related to titanium hydride precipitation.

Fractographic aspect variations with crack orientation were examined. The formation of cleavage and fluted features which generally appear in stress corrosion cracking of titanium alloys, was discussed.

References

6. I. Aitchinson, B. Cox, Corrosion, 28 (1972), 83.