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Anodic oxidation and stress corrosion cracking (SCC) of titanium alloys

Part 1 Factors affecting SCC and their influence on the anodic behaviour of alloy Ti-6Al-6V-2.5Sn

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Uniform and reproducible oxide films were formed on alloy Ti-6Al-6V-2.5Sn by anodic oxidation in aqueous 0.5% H_3BO_3, at 10 mA cm^{-2} and voltages up to 110V; dielectric break down occurred above 120V. A parallelism was found between the effect of environmental factors on stress corrosion cracking (SCC), as reported in the literature and the anodic behaviour, as observed by ourselves: factors that increased susceptibility to SCC (increase in temperature or viscosity, alloying, introductions of Cl^- or methanol, lowering of pH) reduced passivity under anodic polarization, while factors that inhibited SCC (thicker oxide films, high pH, phosphate ions) increased passivity. The passivity was associated both with the presence of the anodic oxide and with a transitory effect of the electric field across the oxide and the oxide-electrolyte interface.

1. Introduction

The adoption of titanium alloys in aircraft and other structures demanding a combination of low weight and high strength has been hindered by stress corrosion cracking (SCC) at stress levels well below design limits. The SCC of such alloys has been, since the fifties, a subject of extensive research, in order to establish adequate prediction and prevention techniques and to clarify the cracking mechanism. A detailed review on the subject has been published recently [1].

Attempts to control the SCC of metals, and of titanium alloys in particular, have been based on various approaches; these include control of the environment (e.g., of the pH [2], addition of inhibitors [3], reducing the water content [4], control of alloy composition [5] or structure [6], control of surface potential [7], formation on the surface of protective layers such as paints [2], sprayed oxide coatings [8], surface alloy layers [9], etc).

In the case of titanium alloys, little work has been done on the possible effect of anodic oxide films on the behaviour of such alloys under conditions that induce SCC. Recent results [10, 11] have confirmed the important role of hydrogen in the SCC of titanium alloys; the influence of oxide films, which slow-down the penetration of hydrogen [12] merits serious consideration.

Although Crossley [13] has reported that anodic oxide films failed to protect titanium alloys (Ti-6% Al-4% V or Ti-13% V-11% Cr-3% Al) against SCC, recent investigations indicate that anodic oxidation may have a favourable influence. Thus, Green and Sedricks [14] reported that anodic films protected titanium alloys under conditions in which samples covered with very thin oxide films failed as a result of SCC. Souffrant [15, 16] showed that specimens (of titanium and other light alloys) covered with anodic oxide films exhibited high resistance to corrosion under conditions inducing stress corrosion cracking, while cadmium coatings failed under the same conditions; however, he states that his tests were not very conclusive since stress levels were too low ($0.8E_{0.2}$) to initiate cracking. Inhibition of SCC by anodic oxidation has also been reported for other light alloys, notably magnesium [17] and aluminium [18]; still, the available data are insufficient for a definitive answer to the problem of the relationship between SCC and the presence of oxide films.

Every attempt to analyse the contribution by any single factor to the SCC of a given alloy must explain the effect of that factor on at least three features of the SCC mechanism [19]: on the energy requirements for fracture, on the fracture kinetics, and on the specific influences of metallurgical and chemical factors. However, in analysing the effect of anodic oxide films the task is simplified, since we may assume that the film would affect only the first (crack initiation) step of SCC, and its effect on crack propagation would be negligible. None of the models currently used to describe the mechanism of SCC in alloys (the mass-transport model [20], the strain-controlled fracture model [21], the mechanical-electrochemical effect model [22] or the hydrogen absorption model [23] deals specifically with the crack initiation stage and the possible influence of surface state on it; indeed, most of the models assume that the environment reacts with the bare metal, without explaining how such a bare surface would be produced.

In the case of titanium alloys (which are normally covered by a "natural" oxide film), existing models that take into consideration the surface state provide better agreement with experimental data on SCC (even if the crack initiation step has not been considered in particular). Thus, Krafft's equation [21] for the stress intensity required for cracking (K_{ISCC}) is based only on bulk properties:

$$K_{\mathrm{ISCC}} = \sigma_{\mathrm{Y}}\, 2\pi\, d_{\mathrm{T}}/(1 - 2v) \qquad (1)$$

where σ_{Y} is the yield stress, d_{T} is a structural term, and v is Poisson's ratio; Equation 1 does not fit well the behaviour of titanium alloys [19]. Better agreement is obtained with Parkin's equation [24] for the SCC susceptibility parameter σ_{Fr}:

$$\sigma_{\mathrm{Fr}} = \sigma_0 + k d^{-1/2} \qquad (2)$$

where σ_0 is a functional constant, d is the grain size and k is defined as:

$$k = [(6\pi G\gamma)/(1 - v)]^{1/2} \qquad (3)$$

where G is the modulus of rigidity, and γ is the surface energy, i.e., a surface parameter is used.

Direct comparative tests of the SCC of titanium alloys with or without anodic oxide films are not usually possible, since such tests require fatigue-precracked samples, and the inside surfaces of cracks cannot be anodically oxidized; moreover, tests on such samples would not provide information on crack initiation, which is the main stage affected by the presence of an anodic film. For that reason, we based our approach on a combination of an indirect evaluation method (which is the subject of this communication) and of SCC tests on notched but not precracked samples, at stress levels that are sufficient to initiate SCC (those would be described in a subsequent paper).

2. Experimental

The anodic oxidation of titanium alloys has not been studied in detail, and little is known about the properties of the anodic films; for this reason, we had to select first the most adequate electrolyte and anodizing conditions for alloy Ti-6Al-6V-2.5Sn (TAVE) (supplied by Ugine) which was used in our study. A Hewlett-Packard 6209B d.c. power supply was used for the anodic oxidation, with continuous plotting of current-time curves on a SEFRAM BGD recorder. Commercial titanium was used as the cathode, at an immersed anode: cathode surface ratio of 2:1, the ratio of immersed anode surface to total electrolyte volume was 10 cm^2:100 cm^3. The oxidation was carried out in open vessels, with the solutions exposed to free contact with air. Deionized water and analytical-grade reagents were used to prepare the various solutions.

A literature search provided a list of factors that influence the SCC of titanium alloys (see Table I); in order to establish a possible relationship between the effect of such factors on the SCC and the anodic behaviour of titanium alloys covered with an oxide film, we kept all other variables constant and only tested the influence of the introduction of a given single factor (among those in the list) during the anodic oxidation. A change in anodic behaviour could be indicated by a variety of parameters (e.g., breakdown voltage of the anodic film, time to reach a given potential drop at constant current, steady-state "residual" current after the film buildup, etc.); the "residual" current was the most sensitive and best reproducible of those, and was thus used by us as an indicator of the influence of the various factors.

The following remarks should be made with respect to some of the investigated factors. Chloride ions: the accleration of SCC by such ions is well established, and several authors

[25, 26] believe that such ions are directly responsible for SCC in both aqueous and methanol solutions. The use of methanol as a solvent: many alloys that are not susceptible to SCC in aqueous solutions are subject to such cracking in methanol solutions, even if unnotched specimens are used [1]. Acidity of the solution: this is somewhat ambiguous, since the pH at the tip of a propagating crack is not necessarily the same as that in the bulk of the solution. The effect of iodide ions on SCC is controversial [1, 26].

3. Results

3.1. Anodic oxidation

Some difficulties were encountered in obtaining reproducible and uniform films on the alloy surface. Electrolytes that are commonly used in the anodic oxidation of unalloyed titanium (sulphuric acid solutions [30, 31], alkali-metal hydroxides [32], mixed nitrates [33], organic acids [34]) either failed to produce an oxide film on the alloy or yielded uneven, patchy films with high residual currents and with poor reproducibility. Satisfactory anodic films were obtained with good reproducibility under the following conditions:

electrolyte – 0.5% H_3BO_3 (in water), at ambient temperature (about 22°C)
surface preparation – degreasing with acetone, etching in sulphochromic mixture
oxidation – at constant current (10 mA cm^{-2}) to the desire voltage, then at constant voltage until the residual current approached a constant value.

Under those conditions the films had a uniform appearance and the residual currents were below 0.01 mA cm^{-2}; breakdown occurred at ~120 V, so that the maximum anodization voltage was 110 V. Breakdown was indicated by current and voltage instabilities, but there was no sparking. An anodic current curve traced under the above conditions is shown in Fig. 1. When the current was switched off after reaching the "residual" low value, the film appearance did not change (i.e., its thickness was substantially unchanged) but on subsequent switching on (after a few seconds) the current assumed a high value, almost equal to that at the end of oxide buildup and its subsequent decrease with time was similar to that observed in the first anodizing. This reversible sequence of decrease-increase-decrease in current could be repeated many times, as shown in Fig. 3. Such behaviour indicated

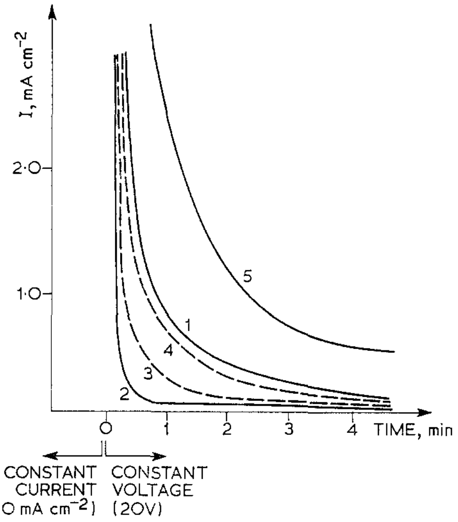

Figure 1 Decrease in current as a function of time at constant voltage.

(1) Alloy TAVE, oxidation in 0.5% H_3BO_3 (aqueous solution).

(2) Titanium (tech. grade), oxidation in 0.5% H_3BO_3 (aqueous).

(3) Alloy TAVE, oxidation in 0.5% H_3BO_3 with pH adjusted to 10 by addition of NH_4OH.

(4) Alloy TAVE covered by anodic film (formed in advance by oxidation at 80 V in the 0.5% H_3BO_3 solution) 0.5% H_3BO_3 (aqueous).

(5) Alloy TAVE, oxidation in 0.5% H_3BO_3 solution in 90% H_2O – 10% CH_3OH mixture.

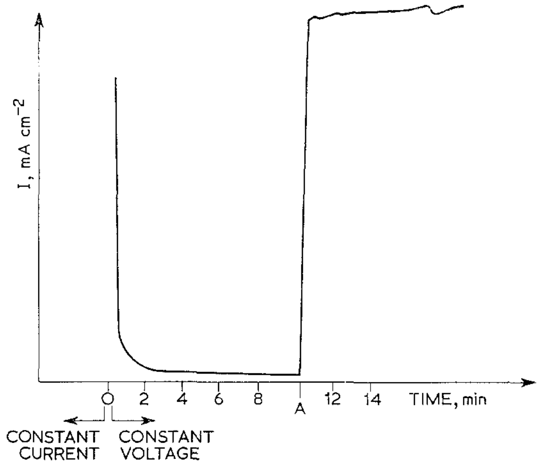

Figure 2 Effect of HCl addition (at point A on time scale) on the anodic current in aqueous 5% H_3BO_3 (alloy TAVE, oxidation at 20 V).

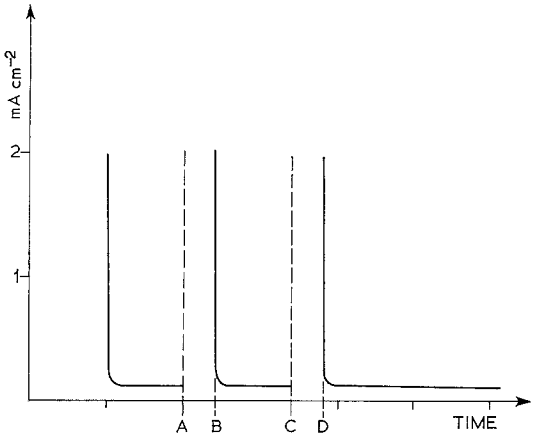

Figure 3 Effect of interruption of the current during the anodic oxidation of alloy TAVE in aqueous 0.5% H_3BO_3. Time scale is intentionally arbitrary; oxidation was carried out at constant voltage (20 V) to a practically constant current, the current was then switched off for 5 sec (point A), switched on again (point B) and the sequence was repeated at points C and D. The spacing between A and B (and C and D) is exaggerated for the sake of clarity.

that the decrease in current (i.e., the passivity induced by anodic oxidation) should not be attributed solely to the presence of the oxide film, but to the combined effect of the film and some reversible field-induced change across the film or at the film-solution interface. Because of the relative rapidity of that change it seems more probable that the change occurs at or near the interface. Commercial unalloyed titanium exhibited similar variations in current upon switching off and on, but there the contribution of the oxide film to passivity was greater.

3.2. Influence of the factors that affect SCC

The influence of the various factors on the residual current is shown in Figs. 1 and 2; for clarity, the results are summarized qualitatively in Table I. We should note that the increase in viscosity was achieved by the use of a 1:1 water: glycerol mixture as a solvent for the boric acid; the introduction of glycerol – an alcohol – could affect the residual current beyond its indirect effect through the increase in viscosity (alcohols are known to affect the SCC of titanium alloys [1]). However, glycerol was also used to increase the viscosity in the SCC tests used as a comparison [27], so that the comparison would still be valid.

4. Discussion of the results

The experimental data show that the passivity (decrease in current at a constant anodic voltage) of the Ti-Al-V-Sn alloy in 0.5% boric acid is only partially caused by the presence of an oxide film, and that reversible changes that are responsible for such passivity occur (probably at or near the oxide-electrolyte interface) when the electric field is applied. A detailed discussion of such behaviour cannot be made on the basis of the available experimental data, and would probably require the use of fast-response electrochemical and recording equipment. In particular, a plot of the voltage rise during the film growth should be of interest to understand the growth mechanism. Experiments have been initiated on this subject and will be reported later. We could, however, assume that the passage of electric current causes migration of certain species within the oxide film or at the film-solution interface; the accumulation or depletion of such species may be responsible for the formation of an "insulating" level in or near the film, which is destroyed (by dissipation of those species or their diffusion back into that level) as soon as the current is switched

TABLE I Influence of various factors on the stress corrosion cracking and anodic behaviour of titanium alloys

Factor	Influence on SCC (according to the literature)	Ref.	Observed effect on anodic residual current–Ti-Al-V-Sn
Addition of Cl^-	Marked acceleration	1	Sharp increase
Addition of methanol	Acceleration	1	Increase
Increase in viscosity	Acceleration	27	Increase
Increase in acidity	Accleration	1	Increase
Heating	Acceleration	28	Increase
Thick oxide film on the metal	Slowed-down	14	Decrease
Alloying of titanium	Acceleration	1	Increase
Addition of iodide	Irregular	1, 26	Irregular
Addition of phosphate	Inhibition	29	Decrease

off. Dyer [35] suggested that the migrating species may be TiOOH; the presence of TiOOH in the anodic oxide on titanium alloys was recently observed by ourselves [unpublished results, with C. Rocques-Carmes and M. Slodzian] by mass-spectrometric analysis secondary emission upon bombardment with argon ions, and this confirms Dyer's views. However, other factors of completely different nature (for example, electrostriction which according to Sato's calculations [36] may even induce structural changes in anodic oxide films) may also be responsible for the observed phenomena, and capacitance effects should not be ruled out.

A striking analogy between the effect of many factors on the SCC behaviour on one hand and the anodic behaviour of titanium alloy Ti-6Al-6V-2.5Sn stands out from the experimental results; the factors that are known to increase the susceptibility to SCC reduce passivity upon anodic polarization, and vice versa. The conclusion may be drawn that the inhibiting or promoting effect of a given factor on the SCC is associated, at least partially, with a hindering or facilitation respectively of the passage of anodic current from the metal to the electrolyte. Our observations indicate that the effect of anodic oxidation is more complicated than the simple formation of a barrier to ionic or electron transfer but the above-mentioned analogy shows that SCC of titanium alloys could be affected and possibly controlled under certain conditions by the formation of anodic oxide films. Moreover, it would probably be possible to use simple residual current measurements (under anodic polarization) in order to provide a comparative, qualitative evaluation of the SCC tendency in a given medium.

5. Summary

1. Electrolytes commonly used for the anodic oxidation of titanium failed to produce satisfactory oxide films on a Ti-Al-V-Sn alloy; uniform oxide films were produced on that alloy by anodic oxidation in 0.5% H_3BO_3 at voltages up to 110 V (breakdown occurred at 120 V).
2. The decrease in current in the above solution was to some extent reversible, ie, despite the presence of the anodic film the anodic current curve plotted upon second or subsequent anodic polarization was practically identical to that plotted during formation of the film, indicating the occurrence of reversible changes as a result of the passage of current.
3. Environmental factors that inhibit SCC of titanium alloys reduced the residual current under anodic polarization, while factors that accelerate SCC increased that current. Thus, the hindering or facilitation of the passage of anodic current is probably responsible, at least partially, for the inhibition or acceleration respectively of SCC of titanium alloys.

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