

EFFECT OF APPLIED POTENTIAL ON THE CORROSION FATIGUE CRACK GROWTH RATE IN TITANIUM ALLOYS

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ABSTRACT

The corrosion fatigue crack growth (FCG) behavior of titanium alloys BT20 (near- α) and TC6 (β) in aqueous solutions of NaCl, NaOH, KOH, H_2CrO_4 , $FeCl_3$ etc., effect of applied potential on the corrosion FCG rates, and fracture surfaces are investigated. It is shown that, depending on the solution composition, the corrosion FCG rate can be either higher or lower than that in the air. Cathodic polarization reduces the crack growth rate in most solutions investigated, however, cathodic polarization sharply increases (by tens or more times) the crack growth rate under corrosion fatigue (CF) of alloys in (0.5-2)M H_2CrO_4 +(0.01-0.1)M NaCl and 0.6M $FeCl_3$ solutions, if the maximum stress intensity exceeds some critical value K_{max}^{HIC} , characteristic of each particular system "alloy-electrolyte". Critical values of K_{max}^{HIC} and the corresponding crack growth rate $(da/dN)_{cr}$ depend on the value of the applied potential as well as the stress ratio, and they represent quantitative characteristics of the role of hydrogen induced cracking (HIC) and local anodic dissolution in CF crack propagation.

KEYWORDS

Titanium alloys, corrosion fatigue, crack growth, potential, fracture surface, hydrogen induced cracking, local anodic dissolution.

INTRODUCTION

For over twenty years, the attention of many researchers throughout the world has been focused on the problem of increased susceptibility of titanium alloys to environment assisted cracking (EAC), i.e. stress corrosion cracking (SCC) and corrosion fatigue (CF), given stress concentrators are like the fatigue crack. Despite the wide scope of the investigations conducted in these years (Bomberger et al., 1985), there is still no single opinion concerning the EAC mechanism of titanium alloys. This problem is discussed in literature, the main point of discussion being the role of two processes as possible mechanisms, namely, the hydrogen induced cracking (or hydrogen embrittlement) and local anodic dissolution (LAD) of metal at the crack tip. In favour of the hydrogen induced cracking (HIC), there are such indications as high tendency of titanium towards formation of brittle hydrides, more intensive EAC of titanium alloys after preliminary hydrogen

absorption, and similarity of fracture surfaces resulting from EAC and HIC of titanium alloys in the hydrogen environment. As anodic polarization accelerates, while cathodic polarization, as a rule, reduces crack growth during EAC of titanium alloys, many investigators suppose the LAD of titanium at the crack tip to be the main mechanism of crack propagation.

The paper (Marichev, 1985) formulates the conditions, the fulfillment of which makes HIC the main mechanism of crack growth under SCC. Since the kind of loading does not restrict these conditions, and titanium alloys are susceptible to internal hydrogen embrittlement (i.e., one of the conditions, depending on the nature of the material, is satisfied), one can assume that there exist such systems "titanium alloy-electrolyte", in which, under certain conditions, HIC will be the main mechanism of corrosion FCG, and the increase of FCG rate under cathodic polarization will be characteristic of these systems. The aim of the present investigation is to verify this assumption.

MATERIALS AND EXPERIMENTAL PROCEDURE

The chemical composition and mechanical properties of the investigated alloys are given in Table 1. The specimens sized 210x25 mm were cut from hot-rolled plates of 8 mm thick for BT20 alloy and 3 mm thick for TC6 alloy. BT20 alloy specimens were tested in the state, in which they were supplied, and TC6 alloy specimens were water quenched from 973 K, and then aged at 753 K for 10 h. The central part of the specimens were ground, and the specimens were precracked to 6 mm (notch + pre-crack) from a side V-notch. Corrosion fatigue tests were conducted at room temperature using an equipment (Shipilov and Lunin, 1987) allowing the crack propagation to be watched continuously through measuring electroresistance in the central part of the specimen. The specimens were tested under axial loading, the cyclic frequency was 0.1 Hz, the cyclic wave form was triangular, the stress ratio (P_{min}/P_{max}) was 0.5 (exceptions will be given separately). The potential of the specimens was measured and controlled using a Ag/AgCl reference electrode, platinum wire serving as a counter electrode. All potentials were converted to the standard hydrogen electrode (SHE). After corrosion fatigue testing, the fracture surfaces of the specimens were examined with a scanning electron microscope (SEM).

Table 1. Chemical composition (wt%) and mechanical properties of titanium alloys.

Material	Structure	Al	V	Mo	Zr	Cr	Fe	H, ppm
BT20	near- α	6.5	0.8	0.8	2.5	--	0.3	52
TC6	β	3.0	6.0	4.5	--	10.5	3.0	60

Material	σ_Y , MPa	σ_{UTS} , MPa	δ , %	Hardness, Rc
BT20	870	1000	9	33
TC6	1540	1600	4	38

Tests were conducted in the air and in aqueous solutions of 0.5M NaCl (the open circuit potential -200 mV), (0.1-1)M NaOH (-140 mV) and KOH (-480 mV),

0.6M FeCl₃ (750 mV), (0.5-2)M H₂CrO₄ (950-1100 mV) etc. Sodium chloride solution was selected as a standard one, for which the most data cited in literature were obtained, and NaOH, KOH, FeCl₃ and H₂CrO₄ solutions were selected as passivating ones (Feeny and Blackburn, 1972), in which we expected suppression of the corrosion FCG due to the LAD mechanism, the increase of K_{max} values under which the corrosion FCG is observed, and the increase of HIC role, because the critical hydrogen concentration, which is necessary for HIC, decreases with the increase of the stress intensity factor (Marichev, 1985).

RESULTS AND DISCUSSION

Corrosion Fatigue Crack Growth Rates. When investigating the CF of BT20 and TC6 titanium alloys, it was found that corrosion environment can either increase (0.5M NaCl solution) or decrease (1M NaOH, 1M KOH, 0.6M FeCl₃ and 2M H₂CrO₄ solutions) the FCG rate as compared to that in the air (Fig. 1). The value of $K_{max} = 19 \text{ MPa}\cdot\sqrt{\text{m}}$, at which a sharp increase of the FCG rate takes place in 0.5M NaCl, may probably be taken for the critical K_{max}^{SCC} value reflecting the SCC contribution to the corrosion FCG (Dawson and Pelloux, 1974), under the given conditions $K_{I,SCC} = 26 \text{ MPa}\cdot\sqrt{\text{m}}$. Lower FCG rates in passivating solutions are not caused by the crack blunting due to intensive dissolution of titanium alloys at their tips. On the contrary, high $K_{I,SCC}$ values (e.g., for BT20 alloy, $K_{I,SCC} = 63 \text{ MPa}\cdot\sqrt{\text{m}}$ in 2M H₂CrO₄ and 65 $\text{MPa}\cdot\sqrt{\text{m}}$ in 0.6M FeCl₃, $K_{I,SCC}$ in the air being 45 $\text{MPa}\cdot\sqrt{\text{m}}$) and low values of corrosion FCG rates agree with the known data on high corrosion resistance of titanium alloys in the solutions mentioned. (High corrosion resistance of titanium alloys in 0.5M NaCl is also known, which does not cover, however, the case of low-frequency CF). It seems that during SCC and CF of titanium alloys in passivating solutions, the protecting (passivating) surface films are formed more rapidly, the films showing better mechanical and/or adhesive characteristics, than those during SCC and CF of alloys in 0.5M NaCl.

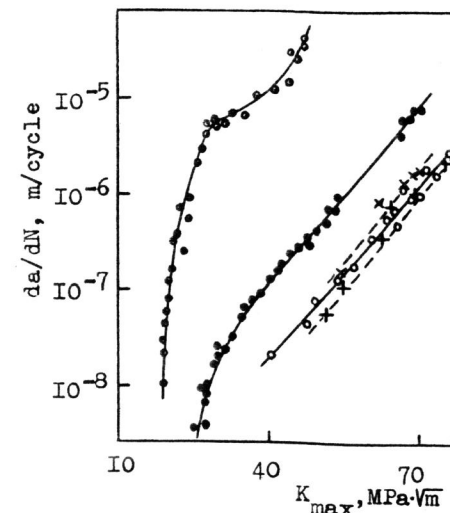


Fig.1. FCG rates for titanium alloy BT20 tested in the air (●) and in 0.5M NaCl (○), 0.6M FeCl₃ (○), 1M KOH (+), 1M KOH+0.03M NaCl (x).

Effect of Applied Potential. When investigating the effect of applied potential on corrosion FCG rate, polarization was set after reaching some initial (corresponding to the open circuit potential) crack growth rate for a period of time needed to register some change in the crack growth rate. Depending on the system "alloy-electrolyte", initial crack growth

rate and applied potential, this period took several seconds or tens of seconds. At this time the crack environment and the conditions of the crack formation did not change markedly, which was indirectly evidenced by the fact that, after polarization switching-off and system's return to the potential equal to the open circuit potential, the corrosion FCG rate took the initial value (exceptions will be given separately). The degree of polarization impact on FCG was evaluated as the ratio the crack growth rate $(da/dN)_p$ under polarization to the initial crack growth rate $(da/dN)_i$ under the open circuit potential.

It was found that short-term (up to 300 s) cathodic polarization decreases the crack growth rate and anodic polarization increases insignificantly it or practically does not influence it upon CF of BT20 and TC6 alloys in 0.5M NaCl, (0.1-1)M NaOH and KOH, (0.5-2)M H₂CrO₄ solutions, i.e. results obtained coincided with the published data (Speidel et al., 1972). Neither displacement of the cathodic potential to the zone of higher negative values, nor electrolyte acidification up to pH 1 resulted in accelerated CF crack propagation in NaCl solution under cathodic polarization. Addition of (0.005-0.1)M NaCl to NaOH and KOH solutions resulted in their weaker passivating capabilities, which manifested itself in some increase of the FCG rate (Fig. 1); however, despite the fact that the weakening of passivating capabilities of a solution contributes to higher hydrogen penetrability of surface films on metal at the crack tip (Marichev, 1985), HIC did not become the main FCG mechanism, since under these conditions cathodic polarization reduced the crack growth rate.

When studying the effect of cathodic polarization on CF crack growth rate for BT20 and TC6 alloys in (0.5-2)M H₂CrO₄ + (0.01-0.1)M NaCl and 0.6M FeCl₃ solutions, existence of critical values was observed for the maximum stress intensity K_{max} ; under lower K_{max} values, cathodic polarization slowed down, and under higher K_{max} values it sharply accelerated the FCG (in tens or more times). Particular values of critical FCG rates $(da/dN)_{cr}$ correspond to critical K_{max} values. Fig. 2 shows that cathodic polariza-

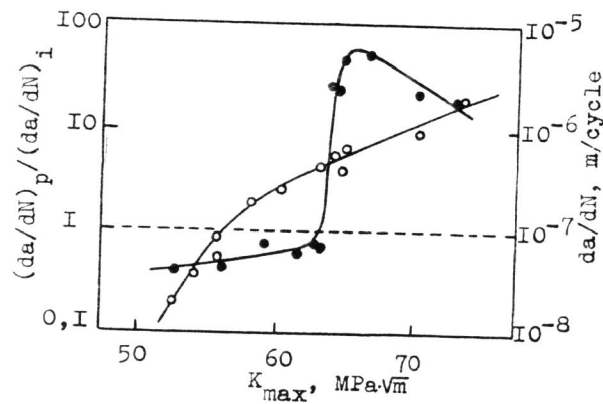


Fig.2. Relationship between the FCG rates (o), the $(da/dN)_p/(da/dN)_i$ ratio (●) for titanium alloy BT20 tested in 0.6M FeCl₃ solution and maximum stress intensity, $R=0.8$, $E_p=-0.2$ V.

tion reduces the FCG rate for BT20 alloy in 0.6M FeCl₃ solution, if $K_{max} < 63.5$ MPa \sqrt{m} and $(da/dN)_i < 4.5 \times 10^{-7}$ m/cycle, and upon reaching these values of K_{max} and $(da/dN)_i$ the same cathodic polarization accelerates the FCG by a factor of 50 and more, other conditions (specimen, electrolyte, kind of loading, temperature, etc.) being unchanged. It should be noted that values of the FCG rate with cathodic polarization, when K_{max} exceeding critical values, reached $(2-4) \times 10^{-4}$ m/cycle and more; therefore, the experiments were interrupted as soon as accelerating action of polarization became evident, and the value of the crack growth rate $(da/dN)_p$ under polarization was determined from crack increment over 3-5 cycles. Immediately after switching-off polarization and the system's return to the open circuit potential, (da/dN) values significantly exceeded initial values $(da/dN)_i$. It was found that upon CF of BT20 alloy in 0.6M FeCl₃, the accelerated crack growth under conditions of cathodic polarization appeared, in a stable mode, after 150 ± 15 s, and when the system was kept under the applied potential with K_{max} lower than the critical value for 300 s, this did not result in FCG acceleration. (The observed FCG slowdown also took place with some time-lag). When testing TC6 alloy under conditions of cathodic polarization, FCG acceleration appeared after 105 ± 10 s. These time-lags seem to reflect the kinetics of a new dynamic equilibrium in the crack when potential is changed, for example, reaching the critical hydrogen concentration, that is required for its growth according to the HIC mechanism, before the crack tip. Time-lags are not connected with the process of cathodic reduction of surface films, since this process would require longer time (Tomashov, 1985) and would not depend on K_{max} value.

Fractography. When investigating fracture surfaces obtained after CF tests of BT20 and TC6 alloys in H₂CrO₄+NaCl and 0.6M FeCl₃ solutions, we could observe, even with small enlargement ratios (x10), essential difference between surface portions, corresponding to FCG under the open circuit potential and accelerated FCG under cathodic polarization, when K_{max} exceeded the critical value. This difference testifies to the change of FCG mechanism under the conditions given above. Fig. 3 shows that characteristic features of the fracture surface under the open circuit potential are ductile fatigue striations, perpendicular to the direction of the crack

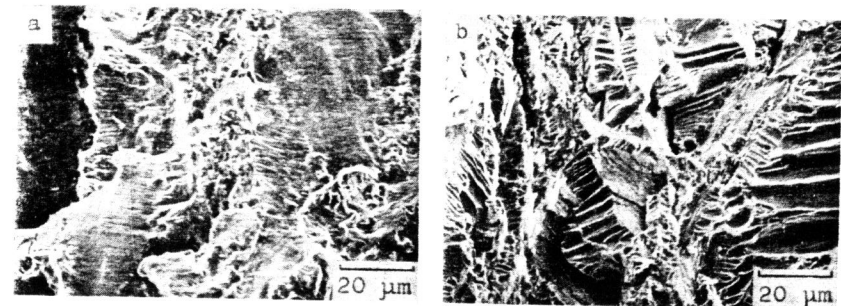


Fig.3. SEM fractographs of titanium alloy BT20 tested in 0.6M FeCl₃ solution at the open circuit potential (a) and at -0.2 V cathodic potential (b): $K_{max}=68$ MPa \sqrt{m} , $(da/dN)_i=8.5 \times 10^{-7}$ m/cycle, $(da/dN)_p=(5-9) \times 10^{-5}$ m/cycle.

growth. Under cathodic polarization, cleavage facets, fragments of "river pattern", secondary cracks, running along the growth direction of the main crack, appear on the fracture surface. These are manifestations characteristic of titanium alloy fracture in the hydrogen environment, i.e., HIC characteristics (Sastrý et al., 1981).

According to views on the SCC mechanism developed in the works (Marichev, 1982, 1985) and the results of electrochemical and fractographic investigations, obtained by the author, the conclusion seems possible that accelerated crack growth in the CF process of BT20 and TC6 alloys in (0.5-2)M H₂CrO₄+ (0.01-0.1)M NaCl and 0.6M FeCl₃ solutions under cathodic polarization, when K_{max} exceeds the critical value, is called forth by the manifestation of HIC mechanism. Therefore, critical values of K_{max}, that should be reached in order that the accelerating effect of cathodic polarization should show itself, are to be regarded as K_{max}^{hic} values, corresponding to the beginning of corrosion FCG according to HIC mechanism: with K_{max}>K_{max}^{hic} and (da/dN)_i>(da/dN)_{cr}, the main FCG mechanism is HIC. Despite the fact that in our experiments FCG rates in FeCl₃ and H₂CrO₄+NaCl solutions were lower than those in the air, it is not improbable that a certain role in CF of BT20 and TC6 alloys in these solutions is played by LAD processes - dissolution "from the passive state" (Tomashov, 1985), since cathodic polarization reduced the FCG rate under K_{max}<K_{max}^{hic}.

So, HIC may be the main mechanism of crack growth upon CF of titanium alloys; however, HIC manifests itself only under specific conditions with abnormally high K_{max} values and very negative potentials of cathodic polarization. It seems that in commonly applied experimental solutions of 0.5M NaCl type, where cathodic polarization always reduces, and anodic polarization increases the FCG rate, the main mechanism of crack growth under CF is LAD; and HIC, caused by the action of corrosion environment, plays no significant role. The conclusion on predominance of some mechanism (HIC or LAD) in corrosion FCG does not, naturally, exclude the possibility of simultaneous and parallel participation of another mechanism, though to a lesser degree.

Effect of Stress Ratio. In order to check, how HIC susceptibility of titanium alloys changes with the transfer from static to cyclic loading, dependence was studied of K_{max}^{hic} on stress ratio R, that was varied from 1 to 0.1. It was found that for equal potentials of cathodic polarization the value of K_{max}^{hic} is lower than the similar K_{hic} value under SCC. For example, in the case shown on Fig. 2, K_{max}^{hic}=63.5 MPa·√m with R=0.8 and K_{hic}=64.5 MPa·√m with R=1. Another peculiarity of HIC manifestation upon CF is the less pronounced accelerating effect of cathodic polarization on the crack growth with low R values, than with high R values or under SCC. For example, under conditions of static loading of a TC6 alloy specimen in 0.6M FeCl₃ solution, cathodic polarization up to E_p=-0.2 V made the crack, that was fixed under the open circuit potential (K_{hic}<K_{Isc}), grow at the rate of over 0.1 m/h, and under CF, as may be seen from Fig. 4, maximum value of the ratio of FCG rate (da/dN)_p to (da/dN)_i rate equalled 70 with R=0.8, 30 with R=0.5 and 5 with R=0.1. With the growing of stress ratio, the increase is seen in both FCG acceleration degree under cathodic polarization and the obtained value of crack growth rate (da/dN)_p. The results obtained lead to the conclusion that HIC under cyclic loading conditions is facilitated and can be observed with lower values of the stress intensity factor, than under static loading conditions. However, the relative HIC contribution (as compared to other competing mechanisms) to the crack propagation upon CF is smaller than upon SCC. It is not excluded that the lower

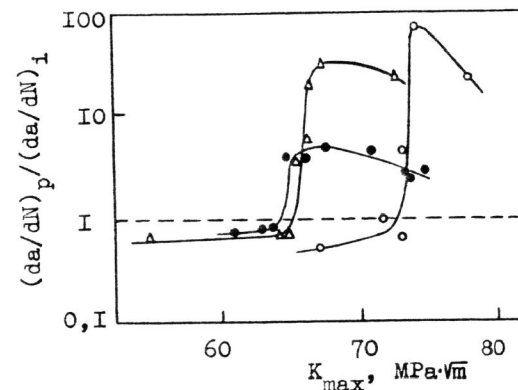


Fig. 4. Relationship between the (da/dN)_p/(da/dN)_i ratios for TC6 alloy tested in 0.6M FeCl₃ and maximum stress intensity for various stress ratio R: 0.1 (●), 0.5 (Δ), 0.8 (○), E_p=-0.2 V.

accelerating action of cathodic polarization on FCG, expressed through the ratio of (da/dN)_p/(da/dN)_i rates, is connected with the increase of the LAD role in CF crack propagation.

CONCLUSIONS

Depending on solution composition, the crack growth rate upon CF of titanium alloys can be either higher (0.5M NaCl solution) or lower (passivating 1M NaOH, 1M KOH, 0.6M FeCl₃ and 2M H₂CrO₄ solutions) than that in the air.

Short-term cathodic polarization reduces, and anodic polarization increases insignificantly or practically does not influence the crack growth rate upon CF of titanium alloys in 0.5M NaCl, (0.1-1)M NaOH, (0.1-1)M KOH, (0.5-2)M H₂CrO₄ solutions.

Cathodic polarization increases, in tens or more times, the crack growth rate upon CF of titanium alloys in 0.6M FeCl₃ and (0.5-2)M H₂CrO₄+(0.01-0.1)M NaCl solutions, if the maximum stress intensity and the corresponding the crack growth rate exceed critical values of K_{max}^{hic} and (da/dN)_{cr}.

Critical values of K_{max} and (da/dN)_{cr} are quantitative indices of the HIC and LAD role in crack propagation upon CF of titanium alloys under conditions of cathodic polarization: when K_{max}>K_{max}^{hic} and (da/dN)>(da/dN)_{cr}, the main FCG mechanism is HIC, and when K_{max}<K_{max}^{hic} and (da/dN)<(da/dN)_{cr}, this is LAD.

HIC under cyclic loading conditions upon CF of titanium alloys is facilitated and can be observed with lower value of the stress intensity factor, than under static loading upon SCC. However, the relative HIC contribution to crack propagation upon CF is smaller, than upon SCC.

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