J. Braz. Chem. Soc., Vol. 8, No. 2, 137-142, 1997.
Printed in Brazil.

Article

An Electrochemical Study of the Crevice Corrosion of Titanium

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Received: June 30, 1996; December 16, 1996

Estudou-se a influência de diferentes fatores na corrosão por fresta em titânio comercialmente puro, em cloreto de sódio, a temperaturas intermediárias. Investigou-se as condições de pH, desarejamento do meio, temperatura e das caraterísticas geométricas da fresta, sob as quais este tipo de corrosão se apresenta. O tipo de íon de titânio que predomina na zona ativa foi determinado como sendo Ti^{3+}. Foram usadas técnicas eletroquímicas e gravimétricas. Pites foram encontrados no titânio apenas a altos potenciais (~5,3V) mas a corrosão por fresta pode aparecer ao potencial de corrosão. A utilização de uma célula de dois compartimentos mostrou que não se pode ultrapassar uma relação máxima entre área catódica e anódica para poder modelar a ativação da superfície metálica dentro da fresta. O desenvolvimento de uma queda ôhmica através dos produtos de corrosão na entrada da fresta é proposto como um fator estabilizador da corrosão.

The influence of different parameters (pH and aeration of the solutions, temperature and geometric features) on the electrochemical behavior of commercially pure titanium in sodium chloride solutions at intermediate temperatures was studied, with the aim of contributing to the understanding of the crevice corrosion susceptibility of this metal. The titanium ion that forms in the active dissolution region was determined bo be Ti^{3+}. Electrochemical and gravimetric techniques were used. Pitting of titanium was found only at high anodic overpotentials (~5.3V), but crevice corrosion can occur at the free corrosion potential. The utilization of a two-compartment cell showed that a maximum ratio of cathodic area to anodic area cannot be surpassed in order to model the activation of the metallic surface in the crevice. The development of an ohmic drop through the corrosion products at the entrance of the crevice is proposed as a stabilizing factor in the corrosion process.

Keywords: *crevice corrosion, titanium*

Introduction

Crevice corrosion is a localized form of corrosion which is very difficult to predict, and which can occur when metallic parts in close contact with non-metallic or other metallic materials are immersed in corrosive solutions, mainly those containing chlorides or other aggressive ions. This type of corrosion has been detected in materials which are normally passive in the studied solutions, as is the case of titanium and its alloys in chloride solutions[1-3]. The first studies of crevice corrosion of titanium in sodium chloride derived from practical problems in the chemical industries, where, due to its excellent resistance to general corrosion, this metal has been extensively employed.

As the electrochemical behavior of titanium in acid solutions has become more investigated[2,4,5], several proposals have been made for the conditions of the solution and the potential inside the crevice. Authors generally agree that the solution in the crevice is deoxygenated, very acidic, and concentrated in the aggressive anions and metallic ions[3]. Some mathemathical models are used to simulate the profiles of the concentration, potential, or current in the crevice[6]. Recently, microelectrodes have been used to measure variables such as pH, current and potential inside the crevice as a function of time[7]. Nevertheless, the reproducibility of crevice corrosion tests is poor, induction times may be long and no satisfactory relation of these times to geometric factors (*i.e.* crevice width and depth, micro- and macro-roughness of the crevice wall), nor to other variables such as temperature and the nature of the material in contact with the metal, has been proposed. Moreover, notwithstanding the fact that the attainment of a critical condition of crevice solution is generally admitted, it is not clear how this condition is stabilized over time.

In this work, crevice corrosion of commercially pure titanium was studied using different electrochemical techniques: potentiodynamic polarization curves, spontaneous activation measurements, electrochemical simulation of crevice corrosion in a two-compartment cell, and the redox potential measurement of the simulated crevice solution. Immersion tests in an autoclave were also performed. Corrosion products were analyzed by Raman spectroscoy, X-ray diffraction, and scanning electron microscopy (SEM).

Experimental

The test specimens of commercially pure titanium were used in block or sheet forms of different dimensions, with the sample areas exposed to the solution varyng from 1 to 12 cm^2. The specimens were polished with silicon carbide paper (from 100 to 2400 grit). For the electrochemical tests, samples were prepared without or with crevices obtained by fastening an acrylic sheet with a Ti screw on the sample surface. For the immersion tests in the autoclave, crevices were produced by tying sandwiches of inert material and titanium plates together with PTFE tape. In the electrochemical tests, the Pyrex cell containing the samples was placed inside a water bath at room temperature or at 50, 70, or 90 °C. The solution used was 1 M sodium chloride prepared with double distilled water, acidified with HCl, so as vary the pH between 0.87 and 6.72. Some tests were made in Na_2SO_4 at pH 6.72. For the deaerated tests, pure nitrogen was bubbled in the solutions. The pH within the crevice was measured with pH-indicating paper after the test. The reference electrode used a the saturated calomel electrode (SCE), and all potentials in the text are referred to it. The equipment used in the electrochemical techniques included a potentiostat (PAR model 174), a programmer controlling the potential scans (BESPW model SMP 72), and an x-t recorder (ECB).

Results and Discussion

Spontaneous activation curves

The effect of the environmental variables (pH, solution temperature, and the presence or absence of O_2) on crevice corrosion was studied by measuring the spontaneous activation time, monitoring the corrosion potential, E_{corr}, as a function of time, of uncreviced samples in NaCl solutions. This type of test evaluates the environmental conditions under which crevice corrosion may take place.

Figure 1 shows the effect of pH on the E_{corr} *vs.* time (t) curves in deaerated medium. It is observed that, for pH 2, for both NaCl and Na_2SO_4, the pre-existent oxide film on the titanium sample tends to dissolve initially. The potential drops to approximately -550 mV, but these solutions seem unable to completely dissolve the film, since the potential soon increases again to less negative values. This increase indicates a new formation or transformation of a passive film, which was confirmed by a change in the superficial color to dark gray. This film formation may be due to a reaction of the metal with water.

At pH 2, dissolution of the oxide film is more effective. In the same figure it can be observed that the potential decay is faster for lower pHs, stabilizing at a constant value of around -720 mV. This kind of experiment in very acid solutions was also carried out by Kelly[2], who observed a change in the slope of the decay curve attributed to a transition from a thin oxide phase to a monolayer of adsorbed species.

In the equilibrium potential-pH diagram at 90 °C presented by Lee[4], the potential value of -720 mV is situated in the Ti^{2+} zone, almost on the border with the Ti^{3+} zone, indicating that Ti may dissolve with the formation of one or both of these species.

The effect of temperature on spontaneous activation was also studied. It was observed that the dissolution of the oxide film became faster as the temperature increased. The stationary potentials were also more negative at higher temperatures, which means that corrosion is more likely as the temperature increases.

Potentiodynamic curves after spontaneous activation

Figure 2 shows potendiodynamic polarization curves obtained after the specimens were previously exposed to

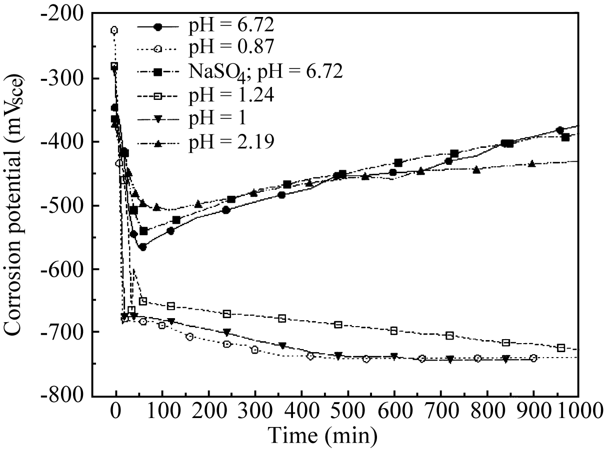

Figure 1. Spontaneous activation curves for uncreviced Ti samples in a deaerated medium for several pHs; T = 90 °C, 1 M NaCl.

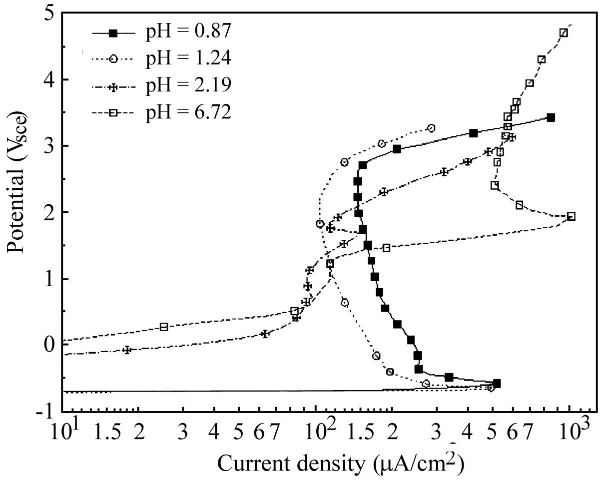

Figure 2. Potentiodynamic curves for different pHs after spontaneous

the solutions for 1000 min, as in Fig. 1. This figure shows the effect of pH on the anodic polarization curves. At pHs less than 2, there is always an active current peak at low potentials. The peak current density, i_m, increases and the corresponding potential, E_m, also increases when the pH decreases, in agreement with Kelly's data[2]. At pHs greater than 2, the active peak is not visible and a second peak appears at higher potentials; this peak potential increases as the pH is raised. A similar peak was observed by Levy and Sklover[5] for commercial titanium in 5% HCl, and was attributed to a secondary active-passive transition. Shibata and Ameer[8] observed a similar peak for zirconium in 1 N H_2SO_4 at 30 °C, which it appears at 1.8 V *vs.* Ag/AgCl. These authors attributed this peak to a phase change in the film that passes from a thin film before the peak to a thick golden film with structural defects after the peak. The reactions that occur in zirconium and titanium may be similar, as they both belong to the periodic group 4.

The temperature did not show any significant influence on E_m, which remained almost constant at -650 mV; i_m, on the other hand increased when the temperature increased, in agreement with results reported by Griess[1] and Kelly[2]. Above 3 V, the current increases more rapidly at higher temperatures. Nevertheless, no pitting was observed in this zone. Thus, it was assumed that the anodic reaction in this zone corresponds to the oxidation of water. Using experimental data for temperatures between 50 and 90 °C, the activation energy for the dissolution of titanium was obtained from the slope of the ln i_m *vs.* 1/T plot; the resulting value (5.3 kcal/mol) is quite low when compared with the value obtained by Kelly in a solution of HCl 0.1 M + NaCl 0.9 M (11 kcal/mol) but his data were obtained at lower temperatures (between 30 and 75 °C) which may indicate some difference in the dissolution path.

Simulation of the crevice conditions in a two-compartment cell

The objective of simulating crevice corrosion conditions in a two-compartment cell is to evaluate the effect of the electrolyte composition, the aeration of the anolyte and catholyte, and the ratio between the anodic area (A_a) and the cathodic area (A_c), on the corrosion process at the anode, under purely spontaneous conditions (without the application of an external current).

For this type of test, two physically separated metal samples (without crevices) were used, which were linked to each other by means of a potentiostat acting as a zero resistance ammeter which maintained the samples at a zero potential difference and simultaneously read the short-circuit current. Both compartments were connected through a salt bridge; one sample was immersed in a NaCl solution, acidified to pH 1 and deaerated with N_2, simulating the crevice environment (anodic sample). The other sample was immersed in a neutral aerated NaCl solution, representing the external surface of the crevice (cathodic sample). The potentials of both samples were independently monitored with the help of high resistance voltammeters and saturated calomel reference electrodes.

Figure 3 presents the variations of the anode (E_a) and cathode (E_c) potentials, and the anodic current density as a function of time. Initially, both samples were passive and showed relatively high potentials, but soon these potentials dropped, showing that anode activation occurred. E_c always remained higher than E_a. The current density accompanied the potential variation. Initially, there was little current circulating, but then the current increased with intense oscillation, which may be attributed to rupture and reformation episodes of the passive film on the anodic surface.

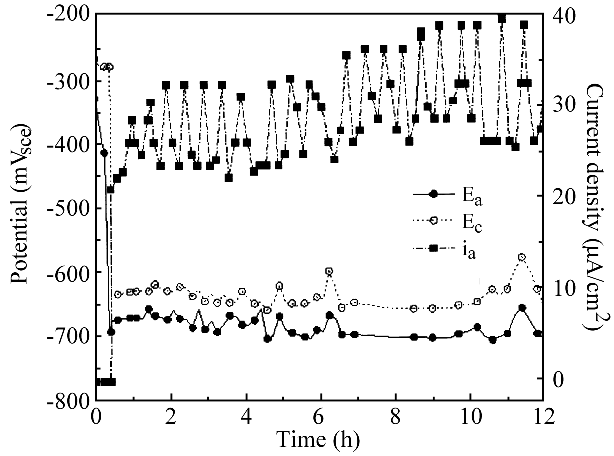

Figure 3. Variation of the anodic and cathodic potential and the anodic current density in electrochemical simulation tests of crevice corrosion in a two-compartment cell (T = 90 °C, 1 M NaCl, and A_c/A_a

Kain and Lee[9] proposed four stages of crevice corrosion. The first (exhaustion of oxygen) and the second (increase of acidity and chloride content) are assumed to have already occurred in the present technique, because an acid and deaerated solution is used in the anodic compartment of the cell. So, only the last two stages are simulated, being the permanent rupture of the passive film and the propagation of crevice corrosion at the anode.

The following area ratios (A_c/A_a) were tested: 8.0; 1.5; 1.0, and 0.6. It was found that for titanium, the ratio should be less than 1 in order for corrosion to set in. Otherwise oscillations between anodic and cathodic current values occur. These results are contrary to those of Rosenfeld and Marshakov who supposed that an increase in the above-mentioned area ratio would always increase crevice corrosion[10]. However, they are similar to those obtained by Kain and Lee for stainless steel[11]. The results may be explained by hypothetical anodic and cathodic polarization curves, considering that reduction of oxygen occurs in the cathodic zone where the pH of the solution is neutral. When A_c/A_a is too high, the cathodic curve should intercept the anodic curve at a potential in the passive zone, and this situation is not expected to lead to crevice corrosion. When this ratio is small, the interception is expected in the active zone of the anode. Another possibility in this second case is to assume that there is a reasonable difference between E_c and E_a , which may correspond to an ohmic drop between the inside and the outside of the crevice, as suggested by Shaw *et al.* for the crevice corrosion of a nickel alloy[12].

It was also observed that corrosion does not take place when the cell compartment containing the anode is aerated, despite a pH of 1, in agreement with the results of Kain and Lee for stainless steels[11]. This confirms that oxygen depletion of the crevice is a necessary step for crevice corrosion in titanium.

Redox potential

Figure 4 presents the redox potential (E_{redox}) of a 1 M NaCl solution, with an initial pH = 1, at a temperature of 90 °C in contact with titanium filings, in a deaerated N_2 medium. This solution represents the one that would be generated by crevice corrosion. E_{redox} becomes more negative with time, attaining a value of -450 mV after 30 h. It should be noted that after 15 h the solution changed from colorless to violet blue, indicating the presence of Ti^{3+}, which should therefore be expected in the crevice, in agreement with the Pourbaix diagram[4] and with the corrosion potential values of Fig. 1, which also point to the presence of Ti^{3+} in the crevice solution.

Discontinuous and continuous cyclic voltammetric curves

Figure 5 shows the discontinuous and continuous cyclic voltammetric curves obtained in 1 M NaCl at 90 °C. Curves 1 and 2 are discontinuous curves with a hold at +5300 mV (with a crevice, a forward scan at v = 1200 V/min and a reverse at v = 120 mV/min) and curve 3 is a continuous one (without a crevice, and with scanning in both directions at v = 1200 mV/min). When the potential was maintained at +5300 mV for 120 min (curve 1), the current density, in spite of decreasing with time, showed fairly high values (higher than 70 μA.cm^{-2}). On reversing the potential scan, the sample repassivated with an oscillating current. After the test, a deep hole was observed in the crevice, shown in the SEM micrograph of Fig. 6.

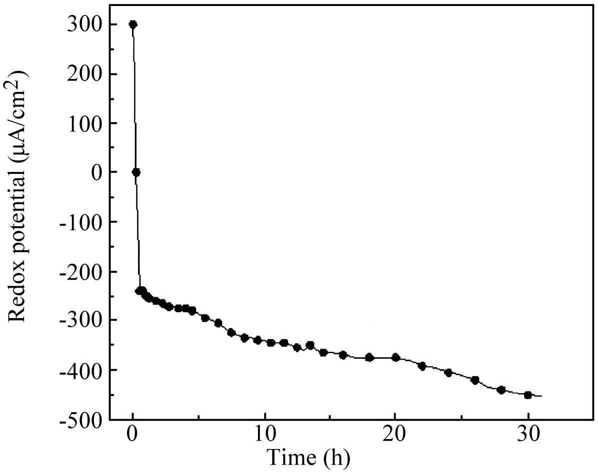

Figure 4. Variation of the redox potential of a deaerated 1 M NaCl solution, pH = 1, in the presence of Ti filings (T = 90 °C).

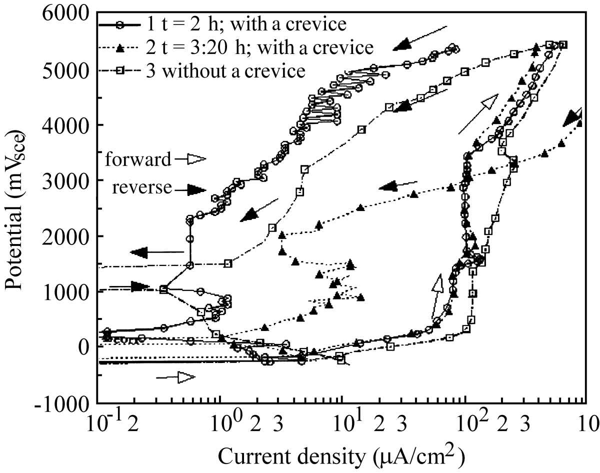

Figure 5. Discontinuous (for creviced sample) and continuous (for uncreviced sample) cyclic voltammetric curves at 90 °C in neutral and aerated 1 M NaCl. The forward scan was at v = 1200 mV/min, and the reverse at 120 mV/min for the discontinuous curves; the forward and reverse scans were at v = 1200 mV/min for the continuous curve. Hold at +5300 mV for 120 min (curve 1) and 200 min (curve 2), and no hold (curve 3).

Curve 2 was obtained by holding the potential at +5300 mV for 200 min. The current increased during the hold.

Figure 6. A scanning electron microscopy image of the interior of the crevice of a sample submitted to discontinuous voltammetry, and held at +5300mV for 120 min.

When the potential scan was reversed, the sample repassivated slowly. At the end of the test there were several holes and some corrosion product in the crevice, and pitting was also observed on the free surface. This potential is therefore higher than or equal to the pitting potential, as pits were formed in the area exposed to the bulk solution. Uhlig and Revie[13] reported a pitting potential of 6.74 V at 90 °C.

The continuous curve 3 presents decreasing currents on the reverse scan. No corrosion was observed, only a surface color change to dark blue, probably associated with a modification in the passivating film. These experiments show that even excursions to high potentials fail to promote instantaneous localized corrosion of titanium, in spite of the presence of a physical crevice. Nevertheless, crevice corrosion is nucleated sooner than pitting at the same potentials.

When the specimen was maintained at +5300 mV for 930 min in the same solution, catastrophic corrosion occurred throughout the whole sample, being more pronounced within the crevice. The pH in the crevice was about 1, and great quantities of corrosion product precipitated. This product was later dried and analyzed. Titanium dioxide in ores can be found in three forms: rutile (tetragonal), anatase (tetragonal), and brookite (orthorhombic)[14]. Raman spectroscopy analysis as well as X-ray analysis of the corrosion product showed features of anatase. Nevertheless, not all peaks could be identified, indicating a more complex nature of the corrosion product. Details of the analysis are given elsewhere[6]. Several authors have tried to identify different forms of TiO_2 by Raman spectroscopy, but the results do not always agree[14].

Weight loss method (immersion tests)

For weight loss tests the specimens were placed inside a PTFE lined autoclave half filled with neutral 1 M NaCl at 100 °C for 15, 30, and 47 days. After the tests, in order to determine the weight loss, the samples were pickled in a 20% HNO_3^- 2% HF solution at 60 °C.

The area used to calculate the corrosion rates, V_c, was only the crevice surface, as no visible attack was found on the external surfaces. For each test, six samples were placed in the autoclave, two of each sandwich type: Ti/acrylic sheet, Ti/PTFE, and Ti/Ti. It was noted that in some cases corrosion did not take place because the crevice was too tight. Mean corrosion rates of ca. 100 mg dm^{-2} day^{-1} (mdd), 200 mdd, and 300 mdd were found for the tests of 15, 30, and 47 days, respectively. The pH in the crevice for times longer than one month was around 1. For the 15 day experiment, the pH measured with paper strips was higher than 2, but as the corrosion had not yet spread over entire the crevice surface, the measured value was probably only a mean value between higher and lower ones. Also the corresponding lower corrosion rate must be attributed to the non-uniform attack of the surface. Note that the corrosion rate is higher as time increases and the solution within the crevice is more acid. For 47 days a very adherent corrosion product obstructed the crevice entrance, which can be attributed to the precipitation of the titanium ions coming from the interior of the crevice as they come in contact with the less acidic solution outside the crevice. This corrosion product represents a barrier between the anodic (inside) and the cathodic (outside) regions of the crevice, and probably leads to a significant ohmic drop, thus stabilizing a potential difference between both regions. It is worth noting that the corrosion rate obtained from weight loss data (equivalent to some hundreds of $\mu A.cm^{-2}$) is much higher than the one extracted from the corrosion current densities in the two-compartment cell simulation. This may be ascribed not only to the 10 degree difference in temperature between the two experiments, but also to the different time scale, besides the distinct physical conditions of the specimens. The double cell experiments were run for only 12 h, and in the autoclave tests it was observed that the mean attack rate was still increasing after 15 days. Yao *et al.*[7] measured current densities in a titanium crevice at 100 °C and obtained data of *c.a.* 30 $\mu A.cm^{-2}$, but their experiments were not conducted for more than 90 h.

Conclusions

The results of the present study confirm certain assumptions made in the literature about the crevice corrosion of titanium in chloride solutions. This form of corrosion can arise at an open circuit potential when Ti forms crevices with acrylic, PTFE, or Titanium itself, at around 100 °C. The principal metallic ion in the crevice solution is Ti^{3+}, the pH of this solution is around 1, and very high corrosion current densities can be found in it. The temperature not only favors the kinetics of active corrosion, but also accelerates the dissolution of the pre-existent passive film.

By means of the simulation technique of the crevice conditions in a two-compartment cell, it was found that the ratio of cathodic to anodic area (A_c/A_a) should be less than 1 for titanium in NaCl in order for crevice corrosion to become established. This result can be better interpreted as the necessity of an appropriate ohmic drop between anodic and cathodic areas to stabilize the crevice corrosion. This ohmic drop, which may be associated with the thick corrosion products protruding from the actual Ti crevices, cannot be properly modeled in the two-compartment cell.

Acknowledgments

The authors wish to thank CNPq and FAPERGS for financial support in the development of this research, and Prof. Sonia R. Biaggio for many helpful comments.

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