

Corrosion of titanium: Part 1: aggressive environments and main forms of degradation

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ABSTRACT

Titanium has outstanding corrosion resistance due to the external natural oxide protective layer formed when it is exposed to an aerated environment. Despite this, titanium may suffer different forms of corrosion in severe environments: uniform corrosion, pitting and crevice corrosion, hydrogen embrittlement, stress-corrosion cracking, fretting corrosion and erosion. In this first review, forms of corrosion affecting titanium are analyzed based on a wide literature review. For each form of corrosion, the mechanism and most severe environment are reported according to the current understanding.

In the second part, this review will address the possible surface treatments that can increase corrosion resistance on commercially pure titanium: Electrochemical anodizing, thermal oxidation, chemical oxidation and bulk treatments such as alloying will be considered, highlighting the advantages of each technique.

Keywords: Corrosion, Crevice, Halides, Pitting, Stress corrosion, Titanium

Introduction

The Reverend William Gregor discovered titanium in 1791 in an ilmenite mineral found in a valley near Manaccan, Cornwall, UK. A few years later, the German chemist Heinrich Klaproth identified the element in rutile ore: he named it *Titan*, after the mythological first sons of the goddess Gaia (Earth in Greek mythology) (1). Nowadays we know titanium to be one of the most abundant metals in the world, constituting about 0.6% of the earth's crust.

Metallic titanium was not used for any field application until 1932, when William Justin Kroll succeed in producing titanium by reducing titanium tetrachloride ($TiCl_4$) with calcium (2). With a density of 4.51 g/cm^3 and mechanical properties comparable to mild steel, titanium has a very high strength to weight ratio: for this reason, since its introduction, it has become a backbone material in the aerospace industry (3). In recent years, thanks to its corrosion resistance, its use has

expanded to other applications, such as power plants, the food industry, petrochemical plants, refineries, heat exchangers, marine structures and medical prostheses (4, 5).

Commercially available titanium is classified depending on its purity and elemental composition. The main classification for titanium is provided by the American Society for Testing and Materials (ASTM). The first 4 ASTM grades of titanium are referred to as "commercially pure" and are not alloyed but only present differences in terms of contents of impurities, especially oxygen (6): grade 1 contains a maximum of 0.18% oxygen while grade 4 has a maximum of 0.40%. Some important alloys (7) were developed to enhance corrosion resistance: grade 7 (Ti grade 2 + 0.12%-0.25% Pd), grade 12 (Ti grade 2 + 0.2%-0.4% Mo, 0.6%-0.9% Ni) and grade 16 (Ti grade 2 + 0.04%-0.08% Pd). Yet, the most commonly used alloy is titanium grade 5, also known as Ti6Al4V, Ti-6Al-4V or Ti 6-4, containing 6% aluminum, 4% vanadium, 0.25% (max) iron and 0.2% (max) oxygen.

Titanium is a very reactive metal: when exposed to an aerated environment, a thin titanium dioxide film, approximately 1.5-10 nm in thickness, is formed. This oxide is usually compact, adherent to the substrate and chemically stable in a variety of environments, and it is responsible for the excellent corrosion resistance of titanium (8, 9).

Despite this, titanium suffers corrosion in aggressive environments. Titanium may suffer both uniform corrosion and localized corrosion: crevice and pitting, hydrogen embrittlement, stress-corrosion cracking, fretting corrosion and erosion.

To overcome these potential issues, specific alloys containing palladium, nickel and molybdenum were introduced.

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These elements promote cathodic reactions, helping the system to reach a passive condition. However, the inclusion of such elements is expensive.

Another possible way is to increase the natural thickness of TiO_2 is by surface treatments (10-24). Oxidation treatments, specifically anodization, have been considered to tune the TiO_2 layer in order to increase its thickness and to obtain a mostly amorphous phase, with the final aim to increase pure titanium corrosion resistance up to the level of more expensive alloys. Thermal oxidation, chemical oxidation and ion implantation are other possible techniques.

The first part of this review is focused on the main forms of corrosion affecting titanium in some common environments. The second part will be dedicated to the available surface treatments used to improve the corrosion resistance of commercially pure titanium.

Uniform corrosion of titanium and its alloys

Mechanism

The nature and composition of the protective oxide covering the surface of titanium depends on the environmental condition in which it is formed. In aqueous environments, the oxide formed is mainly amorphous TiO_2 , with some contributions of other oxidation states, such as Ti_2O_3 and TiO . At high temperatures, rutile, a crystalline and more chemically resistant form of TiO_2 , grows, while intermediate temperatures usually generate less protective oxide, in the crystal form of anatase.

Because of the ease of formation of this protective oxide, corrosion resistance of titanium can be studied by considering the condition under which this oxide is thermodynamically unstable. According to the Pourbaix diagram (pH-potential) of titanium in water (25), titanium is in passive conditions over a wide range of potentials and becomes vulnerable only in strongly oxidizing conditions, where oxide is dissolved, and under strongly reducing conditions, where hydrides are formed. This range is relatively insensitive to chlorides, and for this reason, titanium has an innate resistance in aqueous chloride-containing environments (26).

When titanium is in a passive condition, due to the thin oxidation of titanium surfaces, corrosion rates equal the passive current density: typical values are lower than 0.02 mm/year. This oxide film growth may manifest itself as a colored surface and very slight weight gain by test coupons. The color acquired from the oxide is due to interference between light rays reflected from the oxide and light rays reflected by the oxide and then reflected from the metal underneath, and for this reason, the resulting color is strongly dependent on film thickness (27). Due to the strong passive layer, titanium elements are generally designed without any corrosion allowance (28).

Uniform corrosion occurs in reducing environments, particularly in acidic conditions at high temperature. In strong hot reducing acids, the oxide film is dissolved, and the bare metal is oxidized to soluble trivalent ions ($\text{Ti} \rightarrow \text{Ti}^{3+} + 3e^-$). In the presence of dissolved oxygen in the hot acid, the Ti^{3+} ions are oxidized to Ti^{4+} ions, and the latter subsequently hydrolyzes to form insoluble titanium dioxide. This film may reduce

the corrosion propagation. In the absence of oxygen, when severe corrosion attack has occurred in a reducing hot acid solution, a matt silver-gray surface is observed, due to the formation of titanium hydrides in the film (29).

Titanium corrosion resistance is strongly dependent on the resistance of its protective oxide, which can vary as a function of the surrounding environment. In this section, different common environments in which titanium is used will be reported, together with their effect on the metal.

Seawater

Titanium is reported to be highly resistant to general corrosion in seawater. Titanium does not suffer microbial-induced corrosion (MIC), and although a very small degree of biofouling can be present, no corrosion is found under marine organisms.

In desalination plants, titanium is used in heat exchangers, where the temperature is usually kept around 130°C (8), while titanium is reported to be immune to generalized corrosion up to 260°C. Moreover, it is reported that the metal does not suffer erosion and cavitation corrosion up to 36 m/s in this environment.

These properties make titanium suitable for a variety of applications involving seawater, starting from thin-walled heat exchanger tubing, with consequent good heat transfer properties, up to submarine hulls, ships, platforms, desalination plants, salt production evaporators and water jet propulsion systems (30).

Human body

Due to its biocompatibility, low toxicity, high mechanical strength and low density, titanium is an excellent material for the production of orthodontic, prosthetic and cardiovascular implants (31). All of these devices have to last an entire lifetime immersed in human body fluids without the possibility of inspection and maintenance, and therefore their corrosion resistance is a priority. For this reason, the majority of the literature on titanium's resistance to corrosion is related to human body applications. In this field, the most common solution used to study the electrochemical behavior of the metal is simulated body fluid at pH 7.4 (32). In particular conditions, such as inflammatory states or orthodontic implants in the presence of toothpaste, composition and pH may vary (33).

Titanium biocompatibility is strongly related with its corrosion resistance; in fact, lower corrosion means lower amounts of ions released into the human body, which may lead to prosthesis rejection. Moreover, it is possible to treat titanium surfaces by anodic oxidation, promoting the growth of its oxide, which, if properly tuned, can stimulate the growth of hydroxyapatite, one of the principal components of bone, thus further promoting biocompatibility (34).

The highly desired bone-like apatite formation on titanium is also reported to isolate the metal from the environment, enhancing corrosion resistance (35). Despite the fact that the growth of apatite requires a high degree of surface roughness (31), which may be detrimental for corrosion resistance, other requirements such as the presence of Ca and P ions and the growth of a thicker oxide can be beneficial. Thus ion

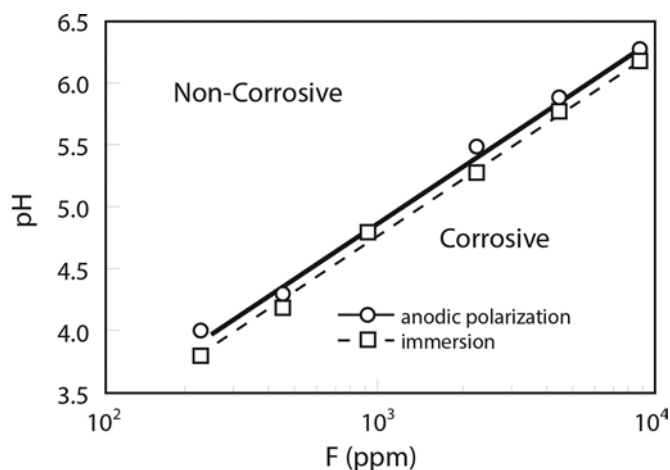


Fig. 1 - Corrosion of titanium as a function of pH and fluoride ion concentration (F): Circles refer to anodic polarization tests; squares refer to immersion tests; ppm = parts per million.

implantation is a common and well-investigated technique to enhance corrosion resistance of Ti (36).

Although very resistant, even titanium and its alloys can suffer corrosion in the human body: The presence of bacterial colonies such as those of *Streptococcus mutans* in the oral environment are known to reduce titanium resistance (37), and fluoride ions present in toothpaste may be very dangerous for titanium, as reported in the next paragraph.

Fluoride-containing environments

Fluoride ions seem to be the only ones able to destroy titanium passivity in aqueous solutions, due to the dissolution of titanium as TiF_6^{2-} and TiF_6^{3-} (30). When passivity is lost, an abrupt increase in corrosion rate or decrease in open circuit potential (OCP) is observed. The transition for each condition is clearly detectable: For instance, Nakagawa et al (38) investigated how the pH threshold for titanium corrosion varies with F⁻ concentration, and they identified a linear correlation between pH threshold and the logarithm of the fluoride concentration (Fig. 1).

Results coming from both anodic polarization and immersion tests were in good accordance. In later investigations (39), the same authors showed the influence of oxygen presence in the solution, reporting a shift in critical pH from 3.8 to 5.1 with 0.05% (weight) of NaF and from 5.5 to 6.0 with 1.0% NaF passing from aerated to deaerated conditions.

Further investigations from Lindholm-Sethson and Ardlin (40) highlighted the existence of 3 different conditions for titanium in fluoride solutions: passive, nonpassive and active. These conditions were revealed by the complex impedance plane of electrochemical impedance spectroscopy (EIS) analyses and suggest the formation of a porous surface film formed at low pH with a large charge-storing ability. The 3 conditions can also be distinguished by the value of final OCP obtained after long exposure to electrolytes with different fluoride content: In the passive condition OCP stabilizes at -0.1 V Ag/AgCl, in nonpassive at about 0.5 V Ag/AgCl, and in the active condition at -1 V Ag/AgCl.

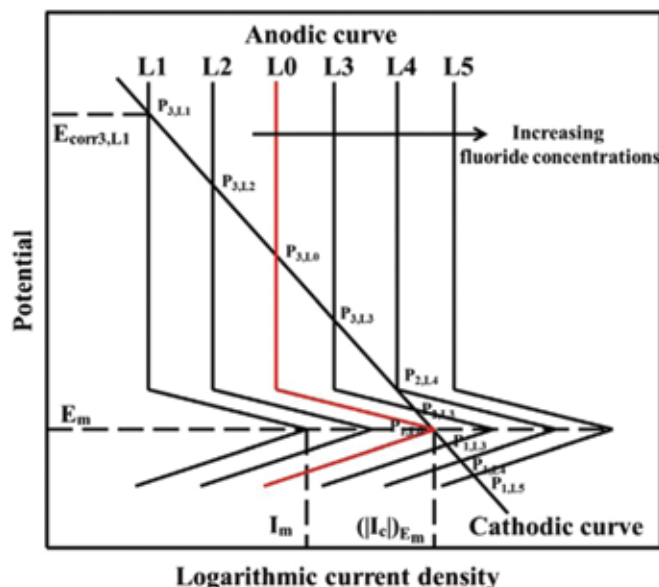


Fig. 2 - L0, L1, L2, L3, L4, L5 stand for ideal anodic polarization curves with fluoride concentration of the critical value, 0 M, 0.0005 M, 0.002 M, 0.003 M, 0.005 M, respectively. $P_{i,j}$ stands for the intersection of the cathodic polarization curve and the single Lj anodic curve, with i = 1 for the intersection in active region, i = 2 for that in active-passive region, i = 3 for that in passive region and j from 0 to 5. $E_{corr3,L1}$ stands for free corrosion potential in passive region (3) of anodic curve L1. E_m is the critical potential to have passivation.

A classification of the corrosion status of titanium in different fluoride concentrations at different pH is reported in Table I.

Another work, from Wang et al (41), investigated the effect of fluoride ions from 0.0005 M to 0.005 M in 0.005 M sulfuric acid solution. This work clarified some aspects of fluoride interaction with titanium oxide. Potentiodynamic polarization tests showed the existence of more than 1 corrosion potential, up to 3 for 0.001 M and 0.002 M of F⁻. This behavior is an indication of unstable passivity, which demonstrates that the system is less stable near the critical value of fluoride concentration at which depassivation actually occurs, which can be explained by Figure 2, representing schematic potentiodynamic curves for fluoride content up to 0.0005 M in H₂SO₄ 0.005 M. In the case of curve L3, corresponding to 0.002 M fluoride concentration, there are 3 intersections of cathodic and anodic curves, in the active, active-passive and passive regions, which reflect the possibility of measuring 3 corrosion potentials in potentiody-

TABLE I - Corrosion conditions in electrolytes with different fluoride concentrations and at different pH

F ion (%)	Electrolyte pH			
	7	5	4.5	4
0	Passive	-	-	Passive
0.3	Passive	Nonpassive	Nonpassive	Active
0.6	Passive	Nonpassive	Active	-
1	Passive	Active	-	Active



dynamic tests. The condition in which the maximum anodic current I_m is equal to the cathodic current ($|I_c|_{Em}$) can be defined as the critical value below which titanium is spontaneously passive and exhibits good corrosion resistance, while above that titanium is in an active state.

Chloride-containing solutions

Hydrochloric acid is a nonoxidizing acid, and therefore, titanium is only moderately resistant to attack in its solutions. The main mechanism of corrosion in HCl is generalized corrosion (42). The corrosion rate increases uniformly with temperature and concentration. At room temperature, titanium is reported to resist up to 5% concentrated HCl (43), and just up to 0.5% at 100°C. Deaerated solutions increase corrosion at lower acid concentrations, but reduce corrosion in concentrations above 10%.

Other chloride-containing solutions become dangerous for titanium only at high temperature. NH_4Cl , for example, causes just 0.004 and <0.001 mm/year of corrosion on titanium at concentrations of 20% and 40% at boiling temperature, but as the temperature is raised to 200°C, corrosion speeds up to 3.9 mm/year at 40% of NH_4Cl (44).

Corrosion rates of titanium in aerated and deaerated hydrochloric acid solutions and in chloride containing electrolytes are reported in Table II (44, 45).

Bromide-containing solutions

The behavior of titanium in hydrobromic acid (HBr) was intensively studied by Heakal et al (46). A small amount of HBr promotes titanium passivation, while higher concentrations destroy the oxide film. The OCP of titanium varies with HBr concentration from -0.3 V Ag/AgCl in the absence of HBr, to more than 0.4 V Ag/AgCl at HBr 1.0 M. This phenomenon is caused by the higher affinity of oxygen to be absorbed on the titanium surface. Accordingly, the oxide film thickness increases, and more positive free corrosion potentials are measured. In more concentrated HBr solutions, bromide ions are adsorbed on the metal surface, displacing oxygen, and partially dissolving the passive layer, leading to an increase of corrosion rate and a reduction of the free corrosion potential.

By calculating the theoretical thickening rates of inner and outer oxide layers, it is found that HBr concentrations higher than 0.5 M start to impede oxide growth. Although a small amount of HBr could be beneficial to titanium passivity, Br ions are more prone to cause pitting than Cl ions (47).

Nitric acid

Nitric acid solutions are strongly oxidizing, so it would be expected that titanium would not suffer corrosion in them. At room temperature, titanium is immune to corrosion up to 65% HNO_3 (8). In hot and pure nitric acid and in condensed acidic vapor, titanium exhibits accelerated dissolution (48).

Corrosion rates at varying nitric acid concentrations and temperatures are reported in Table III.

At high temperatures, titanium corrosion in HNO_3 is at its maximum at concentrations between 40% and 50%; the

TABLE II - Corrosion rates of titanium in HCl- and chloride-containing solutions

Reagent	Concentration (%)	Temperature (°C)	Corrosion rate (mm/year)	
Hydrochloric acid (aerated)	1	35	0.003	
		50	0.006	
		60	0.004	
		100	0.46-2.48	
		Boiling	1.83	
	2	50	0.028	
		60	0.016	
		66	0.61	
		100	7.00	
		6	25	0.07
Hydrochloric acid (de-aerated)	6	50	2.10	
		52	0.68	
		100	44.45	
		37	35	15.00
		1	35	0.003
	3	Boiling	0.0025-2.00	
		35	0.13	
		Boiling	6.10	
		5	35	0.28
		20	35	3.18
Aluminum chloride	5-10	60	0.003	
		100	0.002	
	10	150	0.033	
	25	Room	0.001	
	25	60	Nil	
	25	100	6.60	
	25	Boiling	50.00	
	40	122	100.00	
Ammonium chloride	Saturated	100	Nil	
Calcium chloride	5	100	0.0005	
	55	105	0.0005	
	62	155	Borderline passivity	
Cupric chloride	73	175	0.76	
	1-20	100	0.005-0.0013	
	55	118	0.0025	
Cuprous chloride	50	90	0.0025	
Ferric chloride	1-30	100	0.0008-0.004	
	50	110	0.018	
Magnesium chloride	5	100	0.0008	
	20	100	0.01	
	50	200	0.005	
Manganese chloride	20	100	Nil	
Nickel chloride	20	100	0.004	
Potassium chloride	30	110	0.013	
	Saturated	60	Nil	
Stannic chloride	34	Boiling	0.046	
Sodium chloride	Saturated	Boiling	0.0013	
Zinc chloride	20	104	Nil	
	75	150	0.06	
	80	173	2.10	
	90	250	30.00	

TABLE III - Corrosion rates (mm/year) of titanium in HNO₃

HNO ₃ concentration (%)	35°C	60°C	100°C	190°C	200°C	290°C
5	0.002		0.015			
10	0.004	0.012	0.023			
20	0.0045	0.017	0.0038			0.36
30	0.0069	0.022	0.10	1.5	3.5	
40	0.0058	0.0175	0.05	2.8	5.0	
50	0.0058	0.010	0.18	2.8		
60	0.0071	0.008	0.05	1.5		
69.5	0.011	0.0079	0.019			
70				0.38		1.1
98	0.002					

graph in Figure 3 shows the trend for temperatures from 190°C to 230°C (49).

Unlike many other metals, the higher the impurity level in the acid, the higher is titanium's corrosion resistance; the presence of Si⁴⁺, Cr⁶⁺, Fe³⁺, Ti⁴⁺ ions in nitric acid inhibits high-temperature corrosion of titanium in it.

Titanium and its alloys show good resistance to white-fuming nitric acid, but red-fuming nitric acid can be dangerous, and violent pyrophoric reactions may occur. The reason for this is the formation of a deposit with a finely divided microstructure due to a sort of stress corrosion cracking (8). A small amount of water inhibits this effect, which is no longer observed after the addition of 2% H₂O, as can be seen in Figure 4.

Sulfuric acid

Titanium is commonly used in H₂SO₄ containing environments, from chemical plants to the descaling of desalination plants' heat exchangers (50). At room temperature, it is resistant up to concentrations of 10% (43), but this value decreases rapidly as temperature increases: at boiling point a corrosion rate as high as 9 mm/year is reported in solutions of H₂SO₄ 1% weight (8). From room temperature up to 60°C, the material is attacked with a linearly growing rate up to about 10% concentration, then the corrosion rate grows more slowly with increasing concentration up to 40%, after this value, the corrosion rate decreases, reaching a local minimum at 60%, then restarts to grow rapidly up to a maximum at 80%. At room temperature, purging the solution with nitrogen only slightly affects the corrosion rate, but at higher temperatures, the rate increases catastrophically in deaerated solutions (8). The presence in the solution of a small amount of oxidizing agents or heavy metal ions significantly increases corrosion resistance. As an example, the presence of 0.25% of copper sulfate in 30% H₂SO₄ reduces the corrosion rate to less than 0.1 mm/year.

In Table IV the corrosion rate of titanium in aerated sulfuric acid solutions at different temperatures is reported.

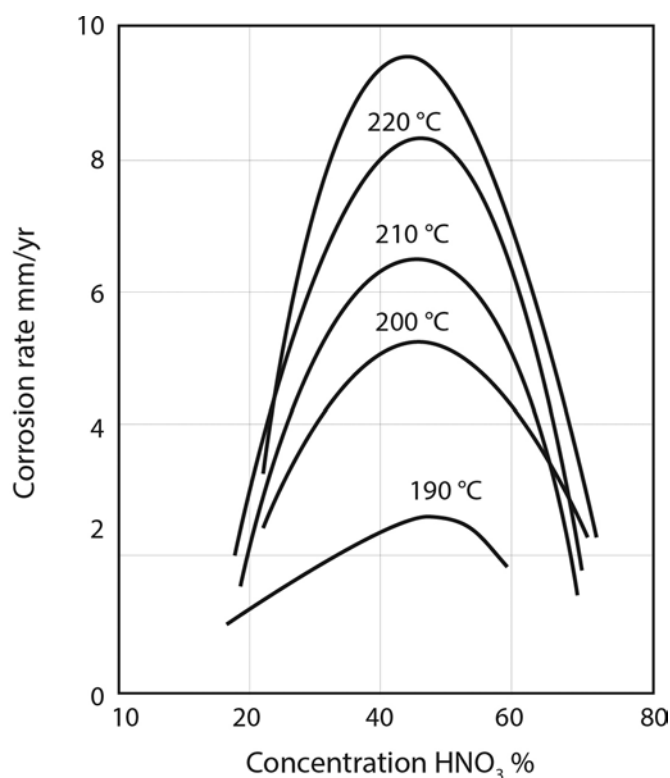


Fig. 3 - Corrosion of unalloyed titanium in high-temperature HNO₃ solutions.

Phosphoric acid

The corrosion of titanium in phosphoric acid increases at increasing temperature and acid concentration. The corrosion rate is lower than that in hydrochloric acid. For this reason, titanium is suitable for use in aerated and deaerated phosphoric acid solutions up to 30% concentration at 35°C. Table V shows the resistance of titanium in phosphoric acid in different concentrations and temperatures (8, 51, 52).

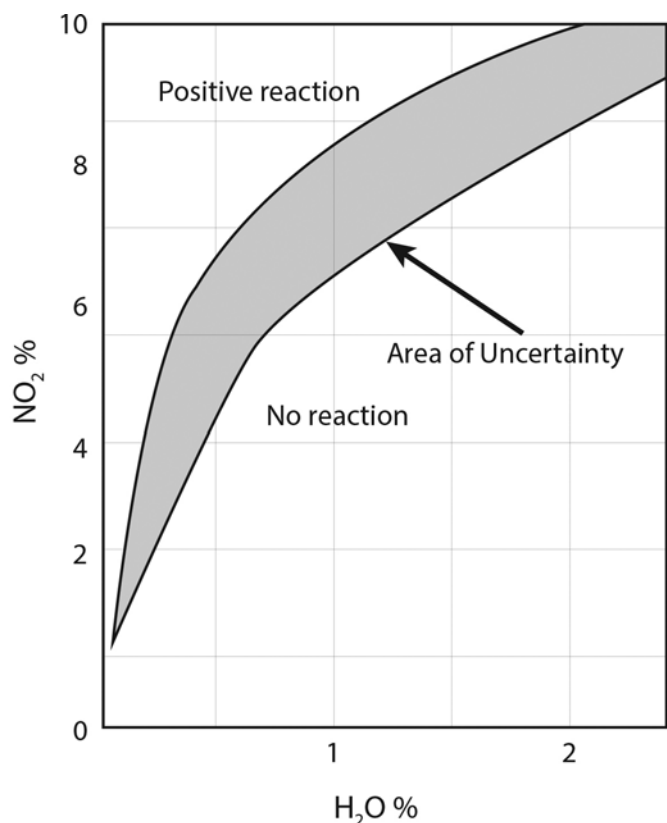


Fig. 4 - Composition limits for avoiding rapid, pyrophoric reactions of titanium in red-fuming nitric acid.

TABLE IV - Corrosion rates (mm/year) of titanium in H₂SO₄ acid

H ₂ SO ₄ concentration (%)	25°C	60°C	Boiling T
1	0.0025	0.008	9
2		0.008	
3	0.005	0.013	
4		1.70	
5	0.0025-0.2 (border-line passivity)		4.8
10	0.25		
40	1.80		
60	0.60		
80	15.00		

Corrosion tests at higher temperature were carried out by Lu (51), who reported a mild corrosion in 1% H₃PO₄ at 250°C with the formation of a thin layer of white corrosion products. Conversely, titanium suffers severe corrosion in more concentrated solutions (10%). Despite the thick layer of corrosion products consisting of titanium oxide phosphate hydrate formed after 24 hours (about 25-µm thick), the corrosion rate is close to 2 mm/year, but is expected to be lower over time

due to the thickening of the corrosion product deposit. At higher acid concentrations, corrosion becomes even faster (52).

Organic acids

Commercially pure titanium and titanium alloys are very resistant to organic acids. Null corrosion can be expected in concentrated solutions of very weak organic acids such as adipic, hydroxyacetic, acetic, terephthalic, tannic, stearic, maleic, tartaric, benzoic, butyric and succinic acids, up to temperatures in excess of 100°C. Corrosion rates can become significant in stronger, deaerated organic acids as acid concentration and temperature increase. Examples of stronger organic acids are formic, lactic, oxalic and trichloroacetic acids (29, 43, 53). In Table VI, the corrosion rates of titanium in different concentrations of different organic acids at various temperatures are reported.

Pitting corrosion

Although the passive oxide film is responsible for titanium’s well-known excellent pitting corrosion resistance, titanium can suffer pitting corrosion in severe working conditions. The susceptibility to pitting corrosion is strongly dependent on temperature and halide ions concentration, the severity of which in general follows the order F < Cl < I < Br (54).

Effect of chlorides

In the presence of chloride ions, a breakdown potential of several volts more positive than the free corrosion potential are necessary (55). Localized corrosion is caused by the migration of the ions across the passive film. Accumulation of oxychloride at the metal–film interface is responsible for the oxide film’s rupture, as a nucleation event (56).

TABLE V - Corrosion rates (mm/year) of titanium in H₃PO₄

H ₃ PO ₄ concentration (%)	35°C	60°C	100°C	200°C	Boiling T
1			0.003	0.001	0.25
2			Nil		0.86
3			0.99		
5	0.0033	0.06	2.36	0.48	3.50
10	0.005	0.09	5.00		
20	0.015	0.33	17.40	55.64	
30	0.018	1.50	26.40		
40	0.33				
50	0.46				
60	0.56				
70	0.66			180	
80	0.74				
85	0.76			>180	



TABLE VI - Corrosion rates of titanium in organic acids at different concentrations and temperatures

Acid	Concentration (%)	Temperature (°C)	Corrosion rate (mm/year)
Formic (aerated)	20	200	0.06
	25	Boiling	2.4
	25	100	0.001
	50	100	0.001
	80	200	20.25
	90	100	0.0013
	10	Boiling	Nil
Formic (deaerated)	25	Boiling	2.40
	45	Boiling	11.00
	50	Boiling	7.60
	50	Boiling	7.60
Lactic	10	100	0.048
	25	Boiling	0.028
	50	100	0.008
	85-100	Boiling	0.01
	90-92	180	0.09
Oxalic	100	Boiling	0.008
	0.5	60	2.40
	1	35	0.15
	1	60	0.45
	1	100	21.0
	5	35	0.13
Trichloroacetic	10	60	11.4
	100	Boiling	14.55

In Table VII, pitting and repassivation potentials in 1 M NaCl with various additions at different temperatures are reported. The presence of oxidizing metal ions can cause severe pitting, as the E_p value follows the sequence: no addition > $FeCl_2$ > $FeCl_3$ > $CuCl_2$. Conversely, the addition of oxygen-containing anions, SO_4^{2-} , SeO_4^{2-} , CrO_4^{2-} and HPO_4^{2-} retards the pitting corrosion of titanium in NaCl (57, 58).

Another interesting method to measure sensitivity to pitting is to study the critical pitting temperature (CPT). By defining solution and potential, the temperature that causes the onset of pitting can be determined, accordingly to studies by Neville and Xu (57). This parameter is reported to be much more reliable than pitting potential, with variations in the order of 0.5°C. CPT is in the range of 80°C to 95°C in HCl solutions with pH 2 and 4, respectively.

Effect of bromides

In bromide-containing solutions, pitting occurs at significantly lower potential than in chloride electrolytes, suggest-

TABLE VII - Pitting and repassivation potentials of titanium in 1 M NaCl with different additions at different temperature

Addition	T [°C]	E_p [V vs SHE]	E_r [V vs SHE]
None	100	passive	passive
	125	3.6	1.0
	150	2.1	1.0
	175	1.8	1.0
	200	1.2	1.0
0.01 M $FeCl_2$	125	passive	passive
	150	1.8	1.3
	175	1.4	0.8
0.01 M $CuCl_2$	125	passive	passive
	150	1.2	0.8
	175	1.0	0.2
0.01 M $FeCl_3$	125	passive	passive
	150	1.7	1.0
	175	1.6	0.7
0.1 Na_2CrO_4	150	2.98	1.16
0.1 Na_2HPO_4	150	2.11	1.32
0.1 $Na_2S_2O_3$	150	1.52	1.21
0.1 Na_2SeO_4	150	2.6	1.22

E_p = pitting potential; E_r = repassivation potential; SHE = standard hydrogen electrode; T = temperature; V = potential.

ing a strong chemical interaction between the TiO_2 surface and Br⁻.

Breakdown occurs at sites with higher oxide conductivity relative to the surrounding film. The phenomenon is chemically specific to Br⁻, so thermal or electrical breakdown is not involved. Casillas et al (47) suggest a mechanism behind pitting corrosion in bromides (Fig. 5). At a potential more negative than the redox potential of the Br/Br₂ couple, +1.2 V Ag/AgCl, the passive film is stable, and only small defects may be present (Fig. 5A). As the potential is raised to values higher than 1.2 V Ag/AgCl, bromide ions are rapidly oxidized at microscopic sites to form bromine gas (Fig. 5B). This process continues until the conductivity of microscopic sites is reduced, probably due to the thickening of the oxide film (Fig. 5C). Between 2 V and 3 V Ag/AgCl, bromide ions are strongly chemisorbed (Fig. 5D), leading to film dissolution and pit growth. Table VIII reports pitting potentials for different bromide-containing solutions (59-61).

Crevice corrosion

Titanium may suffer crevice corrosion in hot chloride solutions (62). In fact, titanium crevice corrosion is highly temperature dependent: for commercially pure titanium, it is generally accepted that crevice corrosion does not take place under 70°C regardless of pH; for pH >10, it occurs regardless

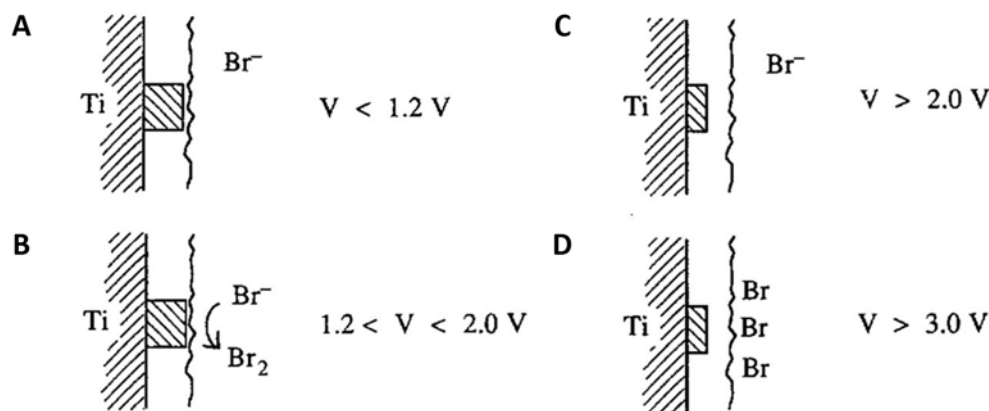


Fig. 5 - Schematic representation of the proposed sequence of events occurring during potential increase on titanium in 1 M KBr, 0.05 M H₂SO₄ (47).

of temperature (30). At temperatures higher than 70°C, crevice corrosion is reported to happen in chloride-, bromide-, iodide-, fluoride- or sulfate-containing solutions (63) only with crevice gaps smaller than 50 μm (64).

Crevice corrosion is divided into 3 stages: initiation, propagation and repassivation. Before initiation, an aerated neutral halide solution is present on both crevice sides. When passivity is locally broken and the oxygen that may repassivate the system is depleted (due to occluded geometry), metal dissolution takes place within the crevice, supported by O₂ reduction occurring on the surfaces external to the crevice. To maintain charge neutrality, halide or sulfate diffuse into the crevice and concentrate as crevice corrosion proceeds.

At the same time, titanium ions hydrolyze, resulting in acidification of the crevice interior and the deposition of corrosion products once neutral conditions are encountered:

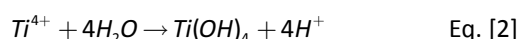
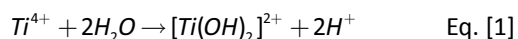


TABLE VIII - Pitting potential of titanium in bromide-containing solutions at ambient temperature

Solution		E _{corr} [V vs SSC]	E _p [V vs SSC]
NH ₄ Br	1 M	-0.33	0.98
	4 M	-0.40	0.90
	sat.	-0.50	-
NaBr	0.01M	-0.55	1.60
	0.1 M	-0.56	1.24
	1 M	-0.56	0.90
	sat.	-0.51	-
Na ₂ SO ₄ 0.5M + 0.8 mg/L BrO ₃ ⁻ + H ₂ SO ₄ (or NaOH)	pH 2.8	-0.47	1.24
	pH 4.7	-0.40	1.39
	pH 7.0	-0.30	1.70
	pH 9.8	-0.20	1.59

E_{corr} = free corrosion potential; E_p = pitting potential; Sat. = Saturated; SSC = Silver Silver Chlorides; V = potential.

In the propagation period, oxygen reduction occurs at the active sites around the crevice. With time, corrosion penetrates into the crevice cavern, the oxygen reduction decreases and the hydrogen evolution increases. At longer times, the corrosion penetration is controlled by the ohmic drop between anodic and cathodic causes. The cathodic reaction produces a local pH increase, leading to a possible repassivation (63).

He et al found a damage function relative to titanium in 0.27 M NaCl at 95°C (65). In the first phase, about 30 days long, the maximum penetration depth, d_{\max} in μm, followed the equation:

$$d_{\max} = 89.74t^{0.87} \quad \text{Eq. [3]}$$

where t is the time in days.

After this period, while corrosion can propagate laterally for a while, the maximum penetration depth does not increase anymore.

The same authors (63, 64) have studied the dependence of crevice corrosion initiation on temperature in 0.27 M NaCl. An abrupt increase in crevice corrosion occurrence occurred for temperatures above 75°C.

The existence of a threshold temperature is explained by the mechanism shown in Figure 6. Above a threshold temperature, close to 65°C, metastable events become possible when a film breakdown and repassivation process starts. This process leads to formation of grain boundaries and more open pathways in the oxide, and consequently corrosion can happen. Under the occluded crevice conditions, cation hydrolysis and development of local acidity occurs. This film degradation process is a precursor to the onset of metastable film breakdown events (65). Once crevice is initiated, propagation is fast, being supported both within the crevice by hydrogen evolution (70%-80%) and outside the crevice by O₂ reduction (30%-20%) (30).

Influence of iron

The content of iron impurities in titanium is reported to have a great effect on crevice corrosion. At low Fe concentration, less than 0.1%, iron is present as intergranular β-phase, and crevice penetration is rapid and limited by the ohmic drop due to the corrosion products' accumulation within the

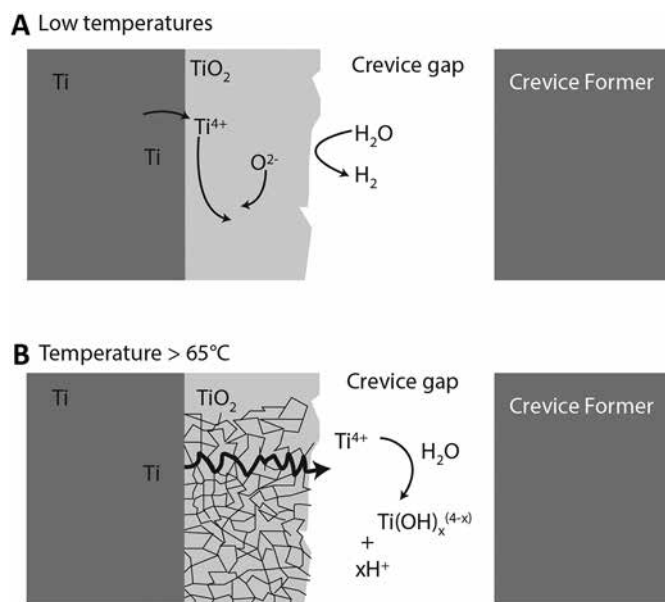


Fig. 6 - Processes occurring in a crevice site: **(A)** low temperature; **(B)** temperature higher than 65°C.

crevice (65). At higher Fe concentration, iron is present in Ti_xFe particles (66). These particles behave as catalytic sites for hydrogen evolution, then increasing the local pH at the propagating sites, reducing corrosion rate and eventually promoting titanium repassivation (67).

Influence of other species

Although oxidizing species (oxygen, chlorine, ferric ions and cupric ions) inhibit uniform corrosion of titanium, most of them can promote the initiation of crevice corrosion and can increase the corrosion's propagation. As these oxidizing species are excellent cathodic depolarizers, they accelerate the cathodic reduction kinetics, which is often the rate-controlling process, and consequently they increase the corrosion rate. These species do not enter into the crevices and then they do to inhibit the corrosion attack. On the other hand, some anionic oxidizing species, such as NO_3^- , ClO_3^- , Cl^- , CrO_3^- , ClO_4^- and MnO_4^- can easily migrate into the crevice gap, and they reduce the corrosion (29).

Environmentally assisted cracking

Stress corrosion cracking

Commercially pure titanium is generally resistant to stress corrosion cracking (SCC) except in a few specific environments, such as aqueous halides (68, 69), nitrogen tetroxide (N_2O_4), anhydrous methanol, red-fuming nitric acid, liquid or solid cadmium and liquid mercury (29).

In general, the mechanisms fall into 2 broad categories: anodic dissolution of the tip of the crack and hydrogen embrittlement. The first mechanism begins at local corroded sites (pits or crevices). In the presence of a corrosion environment and a tensile force applied to the metal, the crack

propagates into the metal, and eventually leads to mechanical failure, if the corrosion rate is not so severe as to allow the rounding of the tip of the crack.

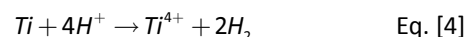
The second mechanism, hydrogen-assisted cracking, is based on the absorption of hydrogen atoms, produced as the first step of the cathodic reaction of hydrogen evolution, near the crack tip. Adsorbed hydrogen permeates inside the titanium, promoting a sort of embrittlement ahead of the crack tip (29, 70).

Hydrogen-induced cracking

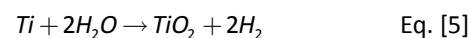
Although SCC takes into account hydrogen adsorption to promote cracking, hydrogen-induced cracking (HIC) requires much more hydrogen to be absorbed by the metal. When hydrogen is absorbed in the metal, it causes embrittlement, depending on the nature of the metal.

In the case of titanium, hydrogen absorption has 2 consequences: the precipitation of a new microstructural titanium hydride phase (71) and the generation of methane gas bubbles due to the chemical reaction with carbon at the grains' boundary (72). In the latter case, failure is due to the growth of voids.

The sources of hydrogen in titanium are multiple: crevice corrosion, once initiated, is supported by reduction of protons inside the crevice Eq. [4], leading to the absorption of hydrogen atoms to produce hydride formation (73).



For passive titanium, corrosion is promoted by reaction with neutral water (according to Eq. [5]) and proceeds at an extremely slow rate, in the range of the passive current density.



In the first step, the generated hydrogen must diffuse through the titanium dioxide film and then must be absorbed at the titanium–film interface. For absorption to proceed, the reduction of Ti^{4+} to Ti^{3+} is necessary. This occurs if a remarkable cathodic polarization occurs, such as in the presence of galvanic coupling with zinc or aluminum, or when titanium is under cathodic protection. When the potential of titanium is brought to values lower than -0.6 V Saturated Calomel Electrode (SCE) (Fig. 7A), the rate of hydrogen absorption increases, reaching very high values for potentials more negative than -1.0 V SCE (74). Above the threshold potential, no hydrogen absorption occurs. At sufficiently negative potential, hydrides are more stable than the titanium; in this condition, the passive titanium dioxide is a sort of diffusion barrier to hydrogen (Fig. 7B).

Once hydrogen reaches the metal under the oxide, its permeability strongly depends on the titanium microstructure. Beta phase is known to have much higher hydrogen diffusivity than alpha phase (75), and also higher hydrogen solubility than alpha phase (at eutectic temperature, 13,200 ppm and 1,500 ppm, respectively). For this reason, HIC in full alpha phase titanium alloys, such as grade 2, is relatively low, while it is much more pronounced in alloys with higher amounts of beta phase, such as grade 12. In these alloys, beta phase

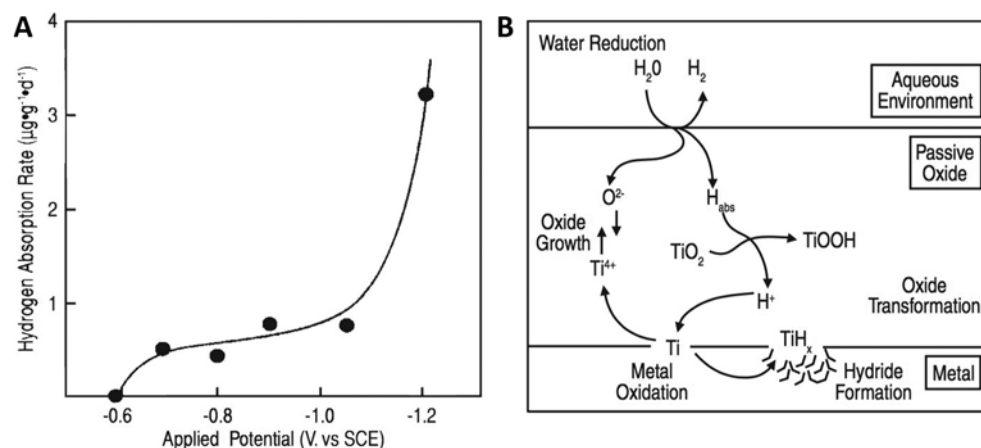


Fig. 7 - (A) Hydrogen absorption rate as a function of applied potential on titanium immersed in artificial seawater at 30°C, **(B)** cathodic reactions occurring in TiO_2 films, after hydrogen absorption (74). SCE = Saturated Calomel Electrode; V = potential.

channels hydrogen toward the bulk material increasing its penetration, then hydrogen precipitates in the alpha phase, promoting crack formation. When beta phase content is high enough, it can dissolve hydrogen, preventing hydride precipitation and secondary cracking.

Conclusions

As discussed in this overview, titanium shows high corrosion resistance in most environments; however, its application in the most aggressive environments makes the development of techniques that enhance this resistance a priority. A summary of some of the more common forms of corrosion was given in this work. As the industrial use of this metal is relatively recent, most of this corrosion-forming mechanism requires further investigation to be completely explained. In the meantime, several treatments to increase corrosion resistance are being developed. The most important will be discussed in the second part of this review.

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