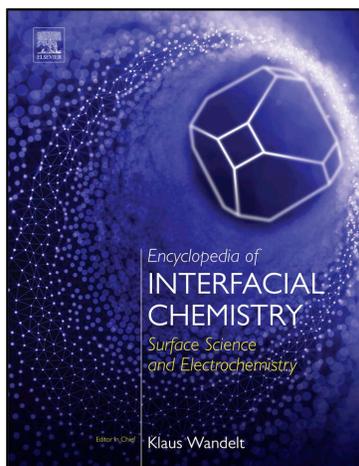


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Corrosion of Titanium and Titanium Alloys

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Glossary

Autopassivation A mechanism for passivating a metal surface by elevating its corrosion potential into the passive region; in this case, the oxidizing power required to raise the corrosion potential is provided by high oxidation state cations of the material undergoing corrosion. The oxidation state of these ions, which were originally produced by the corrosion reaction, is increased by reaction with other oxidants in the solution or on a passive portion of the same metal surface outside of the zone where localized corrosion is taking place.

Cathodic modification A mechanism for passivating a metal surface by elevating its corrosion potential into the passive region; in this case alloying additions of components that are catalytic for the cathodic half-reaction, particularly proton or water reduction, increase the kinetics of the cathodic half-reaction such that the cathodic half-reaction is much faster than the anodic half-reaction at all potentials in the active corrosion region. The only available potential where charge neutrality can be maintained during corrosion (i.e., the corrosion potential) lies within the passive region.

Cation hydrolysis The reaction of metal cations with water to produce metal oxides, hydroxides, or oxy/hydroxy ions. The essential by-product of hydrolysis reactions is protons, which decrease the solution pH.

Critical current density The maximum current density at the peak or “nose” of the active region in the polarization curve for active-passive metals. It is called critical because the cathodic half-reaction or polarizing power supply must supply current density exceeding this value if it is to push the corrosion potential into the passive region and passivate the metal surface.

Dissolution moderators Alloying elements that have high metal–metal bond strengths, in addition to strong metal–oxygen bonds. Having strong metal–metal bonds increases the activation barrier for metal dissolution, while the strong metal–oxygen bonds promote passive film stability.

Flade potential The lowest potential of the passive potential region, where the active-to-passive transition gives way to the passive region.

Passivation potential The potential at the peak or “nose” of the active region in the polarization curve for active-passive metals. The critical current density is measured at the passivation potential.

Passivity Describes the corrosion behavior of a metal surface when the surface reactivity is very low (oxidation current $< 1 \mu\text{A cm}^{-2}$, as a general rule of thumb) due to the presence of a blocking film grown from cations of the metal itself in combination with anions (e.g., OH^- or S^{2-}) derived from the environment. The corrosion rate, while not zero, is low enough that the resultant metal loss is negligible or nearly so in most industrial applications.

Passivity promoters Alloying elements that have a high metal–oxygen bond strength and a relatively weak metal–metal bond; the latter facilitates oxidation and the formation of a three-dimensional oxide layer, which requires the breaking of metal–metal bonds, while the former increases the stability of the passive oxide film formed.

Tafel behavior A current–potential relationship in which the potential has a linear dependence on the logarithm of the current over several orders of magnitude in current. If a plot of the logarithm of the current versus the potential exhibits Tafel behavior, then its slope is an indicator of the reaction mechanism.

Nomenclature

E	Potential (V)
E_m	Passivation potential (V)
$E_{m,d}$	The potential at which the maximum partial current due to metal dissolution is achieved (V)
E_{oc}	Open circuit potential (V)
F	Faraday's constant ($96,485 \text{ C mol}^{-1}$)
H_{abs}	Atomic hydrogen absorbed into the metal matrix
HCP	Hexagonal close-packed
HER	Hydrogen evolution reaction
I_m	Critical current density (A cm^{-2})
$I_{m,d}$	The maximum partial current due to metal dissolution (A)
R	The universal gas constant ($8.314 \text{ C VK}^{-1} \text{ mol}^{-1}$)
T	Absolute temperature (K)

Attributes of Titanium

Titanium, named for the Titans of Roman mythology, is the ninth most abundant element in the Earth's crust. Ti does not occur on Earth in native metallic form; instead, it is found in concentrated form in deposits of rutile (TiO_2), ilmenite (FeTiO_3), and sphene (CaTiSiO_5) and in less-concentrated form in most igneous rocks, iron ores, and the sediments derived from them. It has also been detected in living organisms, meteorites, lunar rock samples, and class-m stellar spectra. Discovered in 1791 by W. Gregor and named in 1795 by M.H. Klaproth, Ti possesses some unusual physical and chemical properties that make it very useful in a broad range of applications. A list of some of the important characteristics of Ti is given in **Table 1**.

Ti metal was first prepared in pure form (99.9%) in 1910 by M.A. Hunter, who heated titanium tetrachloride (TiCl_4) with sodium in a steel bomb, but it remained a laboratory curiosity until 1946 when W.J. Kroll developed the commercial production method of reducing TiCl_4 with magnesium. This process is still in use for producing commercial grade Ti; higher purity Ti is produced by decomposing the iodide.

Ti is an important structural material due to its combination of low density, high strength, and ability to withstand extreme temperatures. It can be as strong as steel but 45% lighter, or twice as strong as aluminum while only 60% heavier. These features have led to its widespread application in the aerospace industry.

Ti is an extremely reactive element. It burns in air and is the only element to burn in nitrogen. Bare metallic Ti reacts strongly with water and hydrogen. This reactivity has been used advantageously in metallurgical processes where Ti is added as a deoxidizer or denitrogenizer, and in ultra-high vacuum pumping where titanium sublimation pumps are used as oxygen getters.

In many common situations, however, this high reactivity actually functions to protect the metal from oxidation. Exposed to oxygen or water, Ti surfaces quickly react to form an oxide that is thin, compact, strongly adherent, and highly insoluble. The

Table 1 Characteristics of titanium

Atomic number	22
Atomic weight	47.867
Specific gravity	4.54 at 20°C
Melting point	1668°C
Boiling point	3287°C
Valence	0, 2, 3, 4
Color	Lustrous silvery metal
Crystal structure ($T < 880^\circ\text{C}$)	Hexagonal close-packed (α)
Crystal structure ($T > 880^\circ\text{C}$)	Cubic close-packed (β)
Specific resistivity	$3 \times 10^{-6} \Omega \text{ cm}$ at 20°C
Stable isotopes	46–50
Radioactive isotopes	39–45, 51–58
Superconductivity temperature	0.53 K
Standard potential	
$\text{Ti}^{2+} + 2\text{e}^- \leftrightarrow \text{Ti}$	–1.63 V vs. SHE
$\text{Ti}^{3+} + \text{e}^- \leftrightarrow \text{Ti}^{2+}$	–2.0 V vs. SHE
$\text{TiO}_2 + 4\text{H}^+ + 4\text{e}^- \leftrightarrow \text{Ti} + 2\text{H}_2\text{O}$	–0.86 V vs. SHE
$\text{Ti}(\text{OH})^{3+} + \text{H}^+ + \text{e}^- \leftrightarrow \text{Ti}^{3+} + \text{H}_2\text{O}$	0.06 V vs. SHE

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thin passive oxide formed then protects the metal from further chemical attack, including that by water, oxygen, moist chlorine, chloride ions, organic acids, and dilute mineral acids. The high reactivity ensures that any mechanical damage to the passive oxide will rapidly repair itself. Thus, Ti, covered by the thin oxide, is highly resistant to gas-phase oxidation and aqueous corrosion, giving it application in many situations where a high level of resistance to chemical reaction is desired, such as in desalination plants, ships, biological implants, kraft mills, chlor-alkali plants, and other aggressive industrial environments.

Titanium alloys can be categorized based on their structure into four main categories, namely alpha (hexagonal close-packed (HCP) structure), near alpha, beta (body-centered cubic structure), and mixed alpha-beta.

Alpha Ti Alloys

This HCP structure is stable at temperatures below 300°C. Titanium can contain substitutional alloying elements like Al and Sn or interstitial elements (C, O, N) that are soluble in the HCP structure of the α -phase and are considered as α -stabilizers. Fe and Mo have very limited solubility in HCP Ti. Due to their excellent corrosion behavior, creep stability, and tensile properties, α -alloys offer better performance at reduced cost and are primarily used in chemical and process engineering. However, their low strength and deformability are of concern.

Near-Alpha Alloys

These alloys are highly α -stabilized and contain only limited quantities of β -stabilizing elements (such as Mo and V). They are characterized by a microstructure consisting mainly of α -phase and containing only small quantities of β -phase. These alloys combine the excellent creep behavior of an α -alloy with the high strength of $\alpha + \beta$ -alloys and are capable of operating at higher temperatures of up to 520°C.

Alpha + Beta Alloys

This group of alloys contains both α - and β -stabilizers and possesses microstructures consisting of mixtures of α - and β -phases. They can be heat treated to high-strength levels and hence are used primarily for high-strength applications at elevated temperatures between 350°C and 400°C.

Beta Ti Alloys

These alloys contain significant quantities of β -stabilizers. The most important feature of beta alloys is that they can be hardened to much higher yield strength than can $\alpha + \beta$ -alloys. While they have a better corrosion resistance than $\alpha + \beta$ -alloys, they also have lower corrosion resistance and higher hydrogen tolerance compared to α -alloys.

Aqueous Electrochemistry of Titanium

The electrochemical response of Ti in aqueous solutions falls somewhere between that of the true valve metals (e.g., Zr, Nb, Ta) and that of the active-passive metals (e.g., Fe, Co, Ni, Cr). Its oxide film formation resembles that of valve metals, while its corrosion is similar to corrosion of active-passive metals.

In aqueous solutions, Ti displays four different types of behavior, termed active, passive, active-passive, and hydrogen evolution; each is exhibited over a particular range of electrochemical potentials in a given environment. Which behavior is spontaneously exhibited at a given time depends on the duration of exposure, pH, temperature, solution composition, material composition, and other factors. The current–potential response of titanium in acidic aqueous solution and the four regions of different behavior are illustrated schematically in Fig. 1.

The cathodic (i.e., reduction) current that flows when a titanium electrode is polarized to a potential within the hydrogen evolution region represents the consumption of electrons by the hydrogen evolution reaction (HER) and a related process, the absorption of hydrogen into the metal. It should be noted, however, that the hydrogen evolution region as depicted in Fig. 1 is an artificial designation applied for convenience in describing the polarization behavior of Ti. In reality, the HER also takes place at potentials throughout the active and active-to-passive transition regions. Indeed, it is a mistake to consider the active and active-passive behaviors on Ti as being separate from the production of hydrogen.

The relatively low anodic current densities (a few $\mu\text{A cm}^{-2}$ or less) displayed by Ti when polarized to potentials within the passive region indicate a very low rate of metal oxidation to produce Ti(IV) ions that may dissolve into solution or participate in oxide film thickening. That the corrosion rate can be very low under such strongly oxidizing conditions is a major advantage for Ti over many other structural metals. This remarkable corrosion resistance of the highly reactive metal depends entirely on the properties of the thin passive oxide film present on the metal surface under these conditions.

The remaining two regions in Fig. 1, the active and active-to-passive transition regions, represent the potential range where Ti is most susceptible to corrosion damage in acidic aqueous environments (although corrosion damage also occurs, along with hydrogen damage, in the hydrogen evolution region).

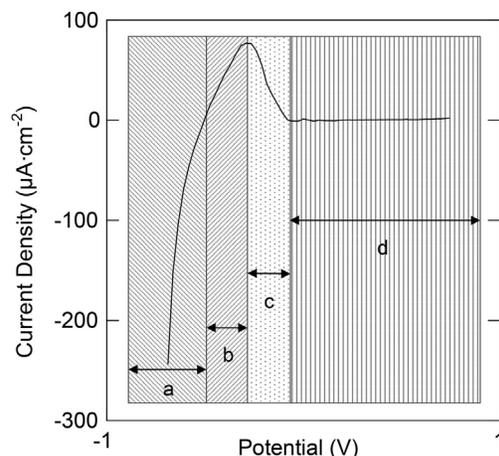


Fig. 1 Schematic illustration of the current–potential relationship for Ti in acidic aqueous electrolyte, indicating the different behavioral ranges: (a) hydrogen evolution region; (b) active region; (c) active-to-passive transition; and (d) passive region. Units indicated on the axes are intended to add perspective to the illustration; they do not represent accurate positioning of the current–potential curve. Reprinted with permission from Noël, J. J. (1999) *The Electrochemistry of Titanium Corrosion*. PhD Thesis, The University of Manitoba, Copyright 1999, James J. Noël.

Active behavior is not exhibited by Ti under all conditions, even when it is polarized to a potential corresponding to what is shown as the active region in Fig. 1. In order for Ti to manifest active behavior, its ubiquitous passive film must be penetrated, either chemically or mechanically, and then the exposed surface must be maintained under appropriate conditions (potential, pH, temperature, dissolved oxygen concentration, and others) so that repassivation does not occur. For Ti, the latter requirement demands an aggressive environment; in deaerated aqueous chloride solutions at 30°C, the maximum pH for which a stable active state exists is about 2.3.

The active region and active-to-passive transition can be characterized as shown in Fig. 2. As the potential is increased from the lower potential limit of the active region, the anodic current density (and therefore the metal dissolution rate) increases to a maximum, called the critical current density, I_m , at the “passivation potential,” E_m . The passivation potential defines the boundary between the active region and the active-to-passive transition. As the potential increased beyond E_m , the anodic current decreases and metal dissolution slows until the active-to-passive transition gives way to the passive region beyond the “Flade potential.”

The effect of having this active-passive maximum in the anodic dissolution rate is that the dissolution rate will be very low if the electrochemical potential at the Ti surface is either much lower than the lower limit of the active dissolution region or higher than the Flade potential. Furthermore, under freely corroding conditions (i.e., without an externally applied potential), the net current on the metal must be zero so that charge is conserved, and the electrochemical potential of the metal must adopt a value at which this

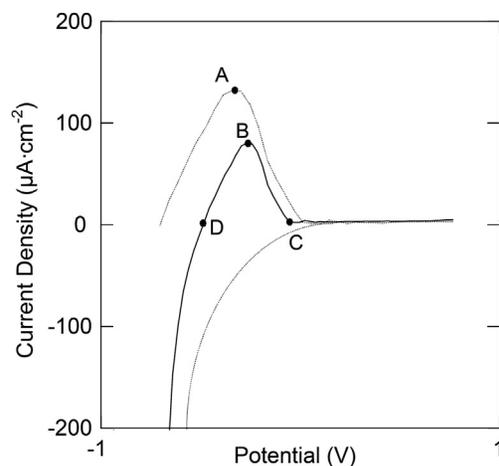


Fig. 2 Schematic illustration of the current–potential relationship for Ti in acidic aqueous electrolyte indicating how the partial currents due to the Ti dissolution and proton reduction reactions (*dotted curves*) combine to yield the observed net current (*solid curve*). Significant points on the curves include: (A) the point at which the Ti dissolution rate is at a maximum ($E_{m,d}$, $I_{m,d}$); (B) the measured current peak, defined by the passivation potential and critical current density for passivation (E_m , I_m); (C) the Flade potential; and (D) the open circuit or corrosion potential, E_{oc} . As in Fig. 1, the units indicated on the axes are provided to add perspective only. Reprinted with permission from Noël, J. J. (1999) *The Electrochemistry of Titanium Corrosion*. PhD Thesis, The University of Manitoba, Copyright 1999, James J. Noël.

condition is satisfied, that is, a potential at which the partial currents due to the oxidation and reduction half-reactions occurring on the surface are equal in magnitude. This is called the corrosion potential, or, more generally, the open circuit potential, E_{oc} . Therefore, if the associated cathodic reaction that drives metal dissolution has a reversible potential greater than the Flade potential and occurs at a rate higher than $I_{m,d}$ at $E = E_{m,d}$ (where $I_{m,d}$ represents the maximum partial current due to metal dissolution and $E_{m,d}$ the potential at which this maximum partial current is achieved), then E_{oc} will be spontaneously driven into the passive region (the only point at which the anodic and cathodic partial currents could be equal in magnitude) and the metal dissolution rate will be exceedingly low.

Two possibilities for the state of the surface in the active and active-to-passive transition regions are that it is covered by either an adsorbed monolayer of oxygen species or by a surface hydride. Under some circumstances, the presence of a hydride phase on the metal is undeniable. The evidence for an adsorbed monolayer of oxygen species in many cases is strong. However, "bare" Ti, or Ti covered by adsorbed water, does not appear to be an option, since one would expect to observe Tafel behavior in the polarization curve under these conditions, as is observed on other water-covered active metals such as Fe. However, anodic Tafel behavior is not observed on Ti.

Throughout the active region and most of the active-to-passive transition (up to $E = E_m + 0.13$ V), Ti dissolves exclusively as Ti(III) ions. Only at the high-potential end of the active-to-passive transition are Ti(IV) ions released from the corroding metal. Stirring has no effect on the dissolution rate in the active and active-to-passive transition regions, indicating that the corrosion reactions are activation-controlled, as opposed to mass transport controlled. The value of E_m is independent of the temperature, while I_m increases with increasing temperature ($\log(I_m) \propto -\frac{1}{T}$). The apparent activation energy for Ti dissolution is 57.3 kJ mol^{-1} in 1 mol dm^{-3} HCl and 59.9 kJ mol^{-1} in 0.5 mol dm^{-3} H_2SO_4 .

Passive Ti spontaneously activates in deoxygenated chloride and sulfate solutions at pH values less than 2.3 and 3.0, respectively, at 30°C . Both E_m and I_m are pH dependent, but to determine the correct functional relationship, E_m and I_m must be corrected for the simultaneously occurring HER. When such a correction is made, yielding the new values $E_{m,d}$ and $I_{m,d}$, the following relationships apply:

$$\frac{\partial \log I_{m,d}}{\partial \text{pH}} = -\frac{2}{3} \quad (1)$$

$$\frac{\partial \ln I_{m,d}}{\partial E_{m,d}} = \frac{F}{2RT} \quad (2)$$

$$\frac{\partial E_{m,d}}{\partial \text{pH}} = -\frac{4}{3} \frac{(2.303)RT}{F} \quad (3)$$

In addition, the lower potential limit of the active region remains nearly constant, while the Flade potential decreases, with increasing pH. The existence of these relationships involving small whole number ratios and multiples of the mechanistically significant parameter $\frac{RT}{F}$ must be accounted for in any reasonable mechanism proposed.

As in any corrosion reaction, the oxidation half-reaction on the freely corroding metal is driven by an electrochemically equivalent amount of reduction, taking place on the same surface or one electrically connected to it, to maintain a charge balance. One of the great corrosion advantages of active-passive metals such as Ti is that, if the cathodic half-reaction is strong enough at potentials corresponding to the active region, the only potentials at which this charge balance can be maintained between the anodic and cathodic half-reactions fall within the passive region. This behavioral feature enables unusual forms of corrosion protection on Ti, including anodic protection (either by impressed current or added strong oxidants) and "cathodic modification," the addition of cathodically catalytic alloying elements (e.g., Ni, Pt, Pd, Ru, etc.) that enhance the cathodic reaction to elevate the corrosion potential into the passive potential range.

One of the extraordinary features of Ti is that its active region corrosion product (Ti(III)) can transform itself into an effective corrosion inhibitor (Ti(IV)) in the same solution, in contact with the corroding electrode, without any special manipulation. Small concentrations of Ti(IV) have been shown to induce repassivation of active Ti. Ti(IV) effects repassivation by acting as an additional oxidant, strengthening the cathodic half-reaction and pushing E_{oc} into the passive region as described earlier. The interesting feature of this process is that the Ti(IV) that aids repassivation can be produced by the oxidation, at passive areas of a piece of Ti undergoing localized corrosion, of Ti(III) ions produced at actively corroding areas on the same piece of metal. The effect has been termed autopassivation. Autopassivation can also occur in any electrolyte-coupled active-passive Ti system; that is, a system in which active state and passive state Ti surfaces are located in the same body of electrolyte (such as that found during localized corrosion).

Active dissolution of Ti under uniform corrosion conditions in sulfate solutions is significantly faster than it is in chloride solutions. The difference has been attributed to the stronger ability of sulfate to complex Ti ions. Ti(III) is very weakly complexed by chloride ($<5\%$ $(\text{Ti}(\text{H}_2\text{O})_5\text{Cl})^{2+}$ in 1.0 mol dm^{-3} HCl). Ti(IV) is complexed more strongly by chloride than is Ti(III), but sulfate complexes are stronger still, the dominant Ti(IV) species in sulfate solutions being $\text{Ti}(\text{OH})_3\text{HSO}_4$. In perchlorate solutions up to 1.5 mol dm^{-3} , Ti(IV) has been found to exist entirely as $(\text{Ti}(\text{OH})_2)^{2+}$ and $(\text{Ti}(\text{OH})_3)^+$ species.

Autopassivation, on the other hand, is more difficult in chloride solutions than in sulfate. It takes 10.5 times as large a concentration of Ti(IV) ions to passivate an active Ti surface in 1.0 mol dm^{-3} HCl than it does in 0.5 mol dm^{-3} H_2SO_4 . It also requires 10–100 times longer to generate the concentration of Ti(IV) required for autopassivation in the HCl solution (due to the lower corrosion rate), suggesting that autopassivation should be much less likely to occur in chloride media. This means that chloride should function to promote localized corrosion, which it is known to do.

Alloying Effects

Small additions of alloying elements can have dramatic influences on the electrochemistry of Ti. Alloying can be used to generate passivity on Ti in two ways: by inhibiting the anodic half-reaction, or by enhancing the cathodic half-reaction. Specifically, alloying with elements that could induce a decrease in the critical anodic current density (I_m) or the passivation potential (E_m) would make it easier for the cathodic half-reaction to exceed a current of $I_{m,d}$ at the potential $E_{m,d}$ and drive E_{oc} into the passive region. Alternatively, alloying with elements that catalyze the cathodic half-reaction, either by increasing the exchange current density or decreasing the cathodic Tafel slope, would also make it easier for the cathodic half-reaction to drive E_{oc} into the passive region by exceeding a current of $I_{m,d}$ at $E_{m,d}$. Alloying to enhance the cathodic reaction rate for this purpose has been termed “cathodic modification.” In either case, it is necessary that the solution contain a redox system with a reversible potential more noble (i.e., higher) than the Flade potential. The H^+/H_2 couple satisfies this condition on Ti.

This cathodic route to passivity must be approached with caution; however, because if the kinetics of the cathodic half-reaction are enhanced, but not enough to exceed $I_{m,d}$ at $E_{m,d}$, the corrosion rate of the alloy will also be increased. This is the case for binary Ti–C alloys containing particles of titanium carbide (TiC), a material on which the cathodic polarization curve in 10% H_2SO_4 at 100°C is “enhanced” over that of Ti, but still intersects the anodic polarization curve of Ti in the active region. Consequently, TiC particles cannot effect passivation of the alloy under these conditions, but instead enhance corrosion. In other cases, the concentration of the alloying element intended to increase the cathodic kinetics may be too low to ensure immediate passivation of the alloy. However, if the alloying element resists corrosion and has low solubility in the corrosive medium, dissolution of the base metal may enrich the alloy surface to the level at which the catalysis of the proton reduction reaction can drive the passivation process.

Alloying elements that can induce passivity of Ti by cathodic modification include Pt, Pd, Ni, Mo, Ru, Re, Fe, Ir, Os, Rh, and Au. Their relative effectiveness is roughly in the same order as their hydrogen overvoltages and exchange current densities for the hydrogen reaction. This relationship between effectiveness and exchange current densities, along with the high corrosion resistance or immunity of most of these elements, make it possible to produce very good cathodically modified alloys on a commercial scale. The low alloy content required (<0.1 wt%) for maximum cathodic modification effect is also critical to the commercial viability because the cost of higher noble metal content would make these alloys uneconomical.

While cathodic modification offers greatly increased resistance to active corrosion of Ti and the alloying additions are often small enough not to significantly influence the mechanical and physical properties of the material, there are some caveats—cathodically modified alloys sometimes suffer increased hydrogen absorption efficiencies and higher passive corrosion rates than unalloyed Ti.

Inhibition of the anodic reaction on Ti lowers the critical current density for passivation (I_m). This is a very different approach to achieving passivity on Ti than the cathodic modification approach. In fact, the two approaches can be used in combination to enhance the ability of Ti alloys to passivate. Alloying elements that suppress the Ti dissolution reaction tend to be those that yield adherent, insoluble oxide compounds, such as Mo, Nb, Cr, W, Zr, and Ta. There are two ways in which alloying elements could act to inhibit anodic dissolution of active-passive alloys, namely, by improving the thermodynamic stability of the metal or that of the oxide. Two groups of alloying elements, the “passivity promoters” and the “dissolution moderators” or “blockers” can be identified based on comparisons of the heat of adsorption of oxygen on the pure elements versus the metal–metal bond energy. Passivity promoters, which include Ti and Cr, are elements that have high metal–oxygen bond strength and a relatively weak metal–metal bond; the latter facilitates oxidation and the formation of a three-dimensional oxide layer, which requires the breaking of metal–metal bonds, while the former increases the stability of the passive oxide film formed. Dissolution moderators or blockers, including Mo, Nb, Ta, W, and Zr, have high metal–metal bond strengths, in addition to strong metal–oxygen bonds. Having strong metal–metal bonds increases the activation barrier for metal dissolution, while the strong metal–oxygen bonds promote passive film stability, as they do for the passivity promoters described earlier.

In practice, it appears that none of these elements is capable on its own of limiting Ti dissolution enough that the hydrogen reduction reaction on Ti can drive the potential into the passive region, unless present in relatively high concentrations. However, complementary additions of cathodically modifying and anodically suppressing elements are effective in promoting passivation of dilute alloys (e.g., ternary alloys such as ASTM Grade-12 Ti (Ti–0.8Ni–0.3Mo), Ti–Pd–Mo, or Ti–Pd–Cr). Unfortunately, the passive corrosion rates on Ti alloys that resist active dissolution can be higher than those on unalloyed Ti. The susceptibility of some of these alloy additions, such as Mo and Cr, to transpassive dissolution results in conversion of the oxide to a more “TiO₂-like” structure at high potentials, which renews the passivity.

Crevice Corrosion

Ti is resistant to most forms of localized corrosion, including pitting (though less resistant in iodide or bromide solutions), intergranular attack, galvanic corrosion (but may suffer hydrogen absorption when Ti is the cathode), and stress corrosion cracking (except in dry methanol). The most dangerous form of localized corrosion to which Ti and its alloys are susceptible is crevice corrosion. Crevice corrosion is an insidious form of corrosion that occurs in cracks and gaps between adjacent metal surfaces, or spaces between metals and other solid materials that hinder mass transport. Crevice corrosion, like pitting, is a type of occluded cell corrosion, that is, corrosion occurs on an area of the metal surface that is exposed to a volume of solution that has stagnated and developed aggressive local chemical conditions due to restrictions in mass transport. A schematic diagram of the processes involved in crevice corrosion on Ti is given in Fig. 3.

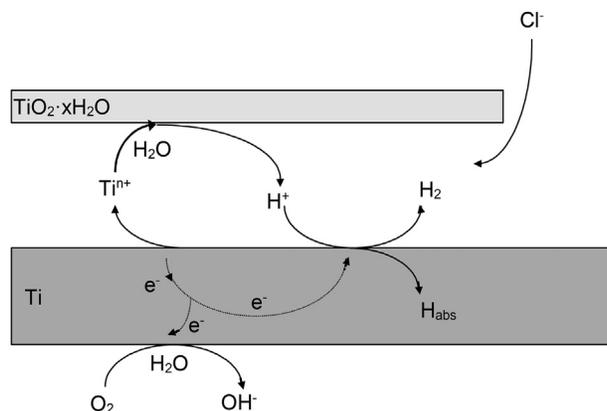


Fig. 3 Schematic depiction of crevice corrosion and the chemical processes involved. Metal oxidation within the crevice is driven by oxygen reduction on the crevice exterior. Metal dissolution is followed by cation hydrolysis, which results in precipitation of corrosion product deposits and acidification of the crevice interior. Once the crevice anolyte pH is low enough, metal oxidation can also couple to proton reduction within the crevice. This is a self-sustaining reaction, producing more protons by cation hydrolysis while other protons are reduced in driving corrosion. The proton reduction reaction leads to hydrogen gas evolution and hydrogen absorption by the metal. Autopassivation by Ti(IV) species is a possibility if active and passive sites coexist within the occluded area. Reprinted with permission from Noël, J. J. (1999) *The Electrochemistry of Titanium Corrosion*. PhD Thesis, The University of Manitoba, Copyright 1999, James J. Noël.

The lifetime of a corroding crevice can be divided into three phenomenological phases: initiation, propagation, and repassivation. Initiation requires that sufficiently aggressive chemical conditions (e.g., low pH, low concentration of dissolved oxygen) develop within the crevice that the passive oxide film is penetrated and the underlying metal can achieve an active state. Propagation, that is, the continuation and spread of crevice corrosion, requires that part of the metal be maintained in an active state (which, in turn, requires specific conditions of pH and potential, as described previously) and part of it be supplied with oxidant. This oxidant can be oxygen or another oxidizing species that is reduced on the passive surfaces of the metal in areas outside of the occluded region, or it can be protons that are generated within the occluded region by hydrolysis of metal ions and reduced to hydrogen within the crevice interior. Repassivation occurs when the chemical conditions or electrochemical potential required for active behavior can no longer be maintained within the crevice, and a passive oxide film is regrown on the corroding surfaces. This could happen as a result of (1) increased mass transport within the crevice (e.g., due to an increase in the crevice gap dimensions), which would cause an increase in the local pH, oxygen ingress within the occluded region, or a change in the potential drop at the metal/solution interface; (2) an increase in the rate of the cathodic reaction, which could generate anodic protection (e.g., autopassivation by Ti(IV) as described earlier); or (3) decreased availability of oxidant.

While this division of the crevice corrosion process into initiation, propagation, and repassivation phases is convenient for descriptive purposes (and these phases must occur in sequence for a given point within a crevice), local initiation, propagation, and repassivation can take place simultaneously at different locations within a corroding crevice throughout its lifetime.

The chemical conditions within a corroding crevice on Ti have been notoriously difficult to measure due to the small volumes of solution and awkward geometries involved and the strongly adherent, insoluble corrosion product deposits produced, yet some attempts have been made using microelectrodes. These investigations showed the depletion of dissolved oxygen within the crevice after immersion in aerated solution and the development of crevice pH values below 1.0 before crevice corrosion initiation in electrolytes having bulk pH values near neutral. The depletion of oxygen within the crevice results from oxygen reduction coupled to metal oxidation, combined with the restricted mass transport conditions that inhibit replenishment of the dissolved oxygen from the bulk solution outside the crevice. Similarly, acidification within the crevice occurs as a result of metal oxidation followed by hydrolysis of the metal cations, for example:



or



The local acidity is maintained by the meager mass transport in and out of the crevice.

It is interesting to note that the two cathodic half-reactions that drive crevice propagation, oxygen reduction and proton reduction, have different influences on the crevice pH. Oxygen reduction takes place on the passive exterior surfaces of a corroding crevice, and in neutral solution creates basic reaction products:



Proton reduction can take place on the interior surfaces of a corroding crevice, which are exposed to acidic solution:



and



where H_{abs} refers to a hydrogen atom absorbed into the metal matrix. Taken alone, reaction (6) would increase the pH of the bulk solution outside the crevice, while reactions (7) and (8) would result in an increase in pH within the crevice. One must recall, however, that reduction reactions are always coupled to an electrically equivalent set of oxidation reactions to maintain a charge balance. In this case, reduction reactions (6)–(8) would be coupled to metal oxidation reactions, all occurring within the crevice and leading to proton-producing hydrolysis reactions such as reactions (4) and (5). Consequently, reaction (6) would have the net effect of lowering the pH inside the crevice, whereas reactions (7) and (8) would have no net effect on the crevice pH, since the amounts of proton production and consumption achieved by coupling reactions (7) and (8) with reactions (4) and (5) are equivalent.

One could imagine the latter internal redox cycle continuing until the Ti was completely consumed, but in practice there are some losses of protons by mass transport out of the crevice, the rates and yields of hydrolysis reactions may change during the crevice lifetime, and, as mentioned earlier, other processes may also lead to repassivation. However, if a small amount of oxygen reduction occurs on exterior surfaces, just enough to balance proton loss from the crevice and maintain the acidic internal pH, significant corrosion damage could be done by the redox cycle involving the coupling of metal oxidation to proton reduction within the crevice. In fact, proton reduction within corroding crevices has been quantified and found to account for ~80%–90% of the damage occurring during periods of crevice corrosion on Ti. In other words, the amount of corrosion observed is 5–10 times the amount directly attributable to the available oxygen.

Finally, in order to maintain charge neutrality in the crevice (where a net oxidation takes place, generating an excess of cationic species in solution), some ionic current must flow between the bulk solution and the crevice anolyte. This is accomplished, at least in part, by migration of anions (e.g., chloride or sulfate) into the crevice. The number of anions required is quite large for a rapidly propagating crevice. Thus, the crevice anolyte rapidly becomes a highly concentrated dense solution. The solution chemistry of Ti in highly concentrated, acidic, saline solutions at elevated temperatures is not well known. It should be noted, however, that the activity coefficient for HCl increases with increasing chloride concentration above $\sim 0.5 \text{ mol dm}^{-3}$, suggesting that the anolyte solution within a propagating crevice could be remarkably aggressive.

Of equal importance to crevice propagation as the aggressive chemical conditions is the maintenance within the crevice of potentials that fall within the active region for Ti (the extent of the active region itself being determined by the chemical conditions). While the potential developed on Ti surfaces exposed to oxygenated solution, including those on the crevice exterior, tends to be high (i.e., within the passive potential range), lower, active region potentials can be established within the crevice due to the combination of current flow and impedance between the crevice interior and exterior. This impedance can result from a combination of oxide film resistance, solution resistance increased by the narrow crevice geometry, film capacitances, etc.

An extensive series of crevice corrosion studies has been conducted on Ti, including the evaluation of the effects of: temperature; oxygen concentration; solution composition and pH; radiation fields; material composition, impurities, and microstructure; heat treatment and welding; crevice tightness; exposure time; and anode-to-cathode area ratios. From both the propagation and repassivation data, it can be concluded that the differences between the behaviors of alloyed and unalloyed Ti indicate that the crevice corrosion of unalloyed Ti is controlled primarily by environmental factors, whereas that of alloyed Ti is governed predominantly by properties of the material itself.

See also: Colored Titanium Oxides: From Jewelry to Biomedical Applications; Corrosion in Pressurized Water; Kinetics of Anodic Oxidation of Aluminum and Titanium: Formation of Porous Alumina and Titanium Oxide Nanotube Layers.

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