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PRODUCT DATA SHEET

Corrosion of Titanium & Titanium Alloys

Titanium Alloys

➤ Introduction

Titanium and titanium alloys owe their excellent corrosion resistance to a stable, protective surface layer of titanium oxide. Titanium metal is highly reactive with oxygen, and the surface oxide forms spontaneously and instantaneously in contact with air and most media. Damage to the oxide film usually heals rapidly if the environment contains oxygen or moisture at the parts per million level. Hence titanium alloys are highly resistant to corrosion, usually corrode at negligible rates and require no corrosion allowance. However, anhydrous or highly reducing conditions may prevent the formation or healing of the oxide film, and corrosion may then become rapid.

This form of corrosion resistance is similar to that of aluminium and magnesium alloys, and of stainless steels, which also rely on a protective oxide film on the surface of a reactive metal.

➤ Alloy Composition Effects

All the commercial purity grades corrode at very low rates while the metal remains in the passive condition. Small contents (< 2 – 3%) of the elements normally present have little effect on the oxide film, and hence on corrosion resistance. However, where the corrosion resistance is marginal (i.e. corrosion rates above about 0.13 mm/year), small amounts of elements such as sulphur and iron accelerate the corrosion rate of the alloy. Minor additions of other elements, such as palladium and nickel, can greatly reduce corrosion under these conditions, and made to highly corrosion resistant alloys such as grade 7.

Weldments of the lean alloys generally show the same corrosion resistance as the unwelded parent metal, without surface treatment. In marginal or active conditions attack may be accelerated at the weld, due to a higher content of impurity elements such as sulphur, iron, oxygen and nitrogen.

➤ General Corrosion

When titanium is fully passive, corrosion rates are typically lower than 0.04 mm/year, due to the highly stable surface protective film. In many environments the film may thicken, which gives interference colours and a slight weight gain. General corrosion may be encountered in reducing acid conditions, particularly at elevated temperatures. In strong and hot reducing acids the titanium oxide film can dissolve, and the unprotected titanium metal be taken rapidly into solution.

➤ Crevice Corrosion

Titanium alloys may suffer crevice corrosion attack by a similar mechanism to that encountered in stainless steels: oxygen depleted reducing acid conditions develop within tight crevices isolated from the bulk corrosion media. Crevice corrosion may be encountered in hot (>70°C) solutions containing chlorides, bromides, fluorides, iodides or sulphates. It can stem from metal to metal joints such as tube to tubesheet joints or badly designed welds, at gaskets, or at surface deposits.

➤ Pitting Corrosion

Titanium alloys are highly resistant to pitting corrosion, and it is rarely encountered.

➤ Hydrogen Damage

Titanium alloys are widely used in environments containing hydrogen, and where impressed currents or galvanic couples generate hydrogen. Hydrogen embrittlement of the titanium may result due to the formation of titanium hydride precipitates, usually without significant reduction of the performance of the alloy. Embrittlement is loss of ductility and toughness of the alloy.

The surface oxide film is a highly effective barrier to the passage of hydrogen, and only traces of moisture or oxygen are effective in maintaining the oxide film. Hence hydrogen embrittlement can usually be avoided. It is unlikely to be encountered at temperatures below about 80°C, or at solution pH between 3 and 12.

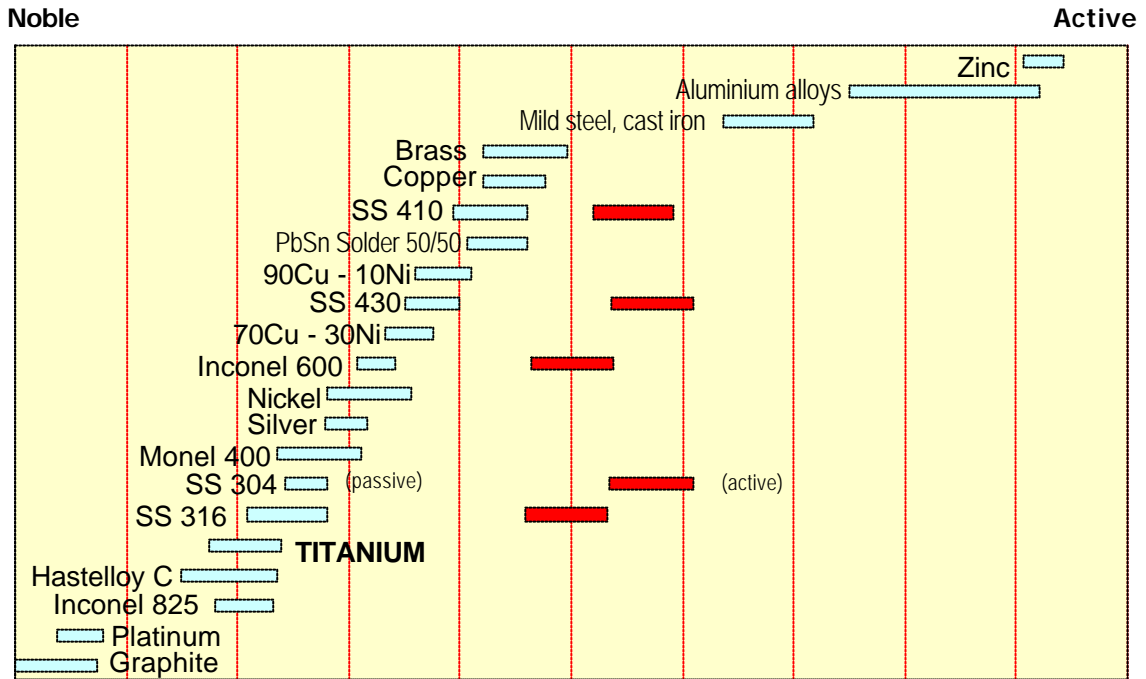
The usual cause of hydrogen damage is excessive hydrogen charging from an impressed current corrosion protection system, or a galvanic couple (see below) with a more active metal, such as aluminium, zinc or

magnesium. Metals which remain passive, such as other titanium alloys, stainless steels, copper alloys and nickel alloys, are unlikely to cause this problem.

➤ **Galvanic Couples**

Titanium rarely suffers accelerated corrosion on coupling with other metals, but it may accelerate the corrosion of a more active metal coupled to it. The rate of attack depends on many factors, including solution chemistry and temperature, and the cathode to anode surface area ratio.

Galvanic series in flowing sea water (2.5 - 4 m/sec, 10 - 27°C)



➤ **Stress Corrosion Cracking**

The commercially pure titanium alloys (grades 1, 2, 7, 11, 12) are immune to SCC except in a few environments, such as anhydrous methanol solutions containing halides, nitrogen tetroxide and red fuming nitric acid. The higher strength alloys have been found susceptible to SCC in aqueous chloride solutions at high stress levels in laboratory tests, but the problem is rarely encountered in practice.

➤ **Erosion Corrosion**

The hardness of the surface oxide film gives excellent resistance to erosion corrosion, which is outstanding compared to most other candidates for heat exchanger service. High flow rates (30m/sec) can be used without problems due to inlet turbulence or pump cavitation effects.

➤ **Corrosion Fatigue**

The highly protective surface oxide film results in insignificant reductions in fatigue strength in water, sea water and most chloride solutions where corrosion is not active.

➤ **Water & Sea Water**

Titanium alloys corrode negligibly in sea water at temperatures up to 260°C. Even under biofouling and deposits, pitting and crevice corrosion are not encountered. Marine atmospheres, splash and tidal zones, and soils also have no effect. Corrosion at tight design crevices may be seen in waters with higher than about 1000 ppm of chlorides at temperatures above about 75°C.

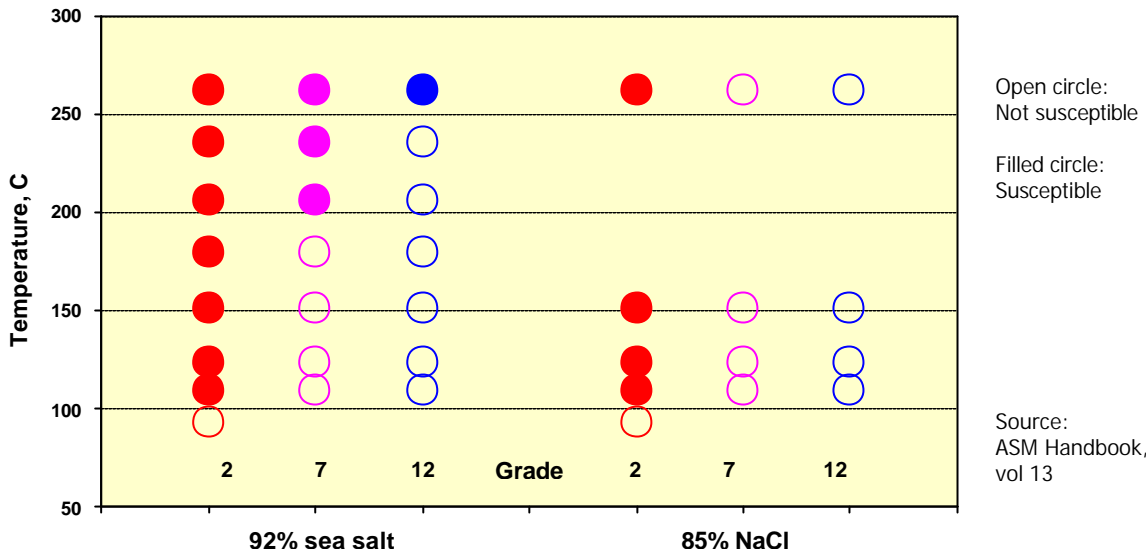
➤ **Oxidising Media**

Titanium alloys are highly resistant to oxidising acids, with corrosion rates typically less than 0.03 mm/year.

➤ **Reducing Acids**

Corrosion of titanium alloys may be encountered when the temperature & concentration of reducing acid solutions exceed critical values, which breaks down the surface oxide layer. Reducing acids include sulphuric, sulphamic, oxalic, trichloroacetic, phosphoric and halogen acids such as hydrochloric and hydrofluoric. Austral Wright Metals can supply detailed corrosion data for these environments.

Guidelines for avoiding localised attack in pressure-bleed tests in the absence of crevices



➤ **Tables of General Corrosion Data** (abstracted from ASM Handbook vol 13.)

This data is for commercial titanium alloys other than the commercial purity grades. The data should be used with care: they provide a general guideline only. Rates depend on the chemistry of the medium, temperature, etc. In situ testing will generally give more reliable data.

Medium	Grade	Conc'n %	Temp °C	Corr'n rate mm/yr
Acetic acid	9	99.7	Boiling	nil
Acetic acid + 5% formic acid	12	58	Boiling	nil
Aluminum chloride	12	10	Boiling	nil
	7	10	100	<0.025
	7	25	100	0.025
Ammonium chloride	12	10	Boiling	nil
Ammonium hydroxide	12	30	Boiling	nil
	9	8, 28	150	nil
Aqua regia	7	3:1	Boiling	12
	12	3:1	Boiling	0.61
	9	3:1	Boiling	1.29
	9	3:1	25	0.015
Calcium chloride	7	62	150	nil
	7	73	177	nil
Chlorine, wet	7	-	25	nil
Chromic acid	7	10	Boiling	nil
	9	10	Boiling	0.008
	9	30	Boiling	0.053
	9	50	Boiling	0.26
Citric acid	7	50	Boiling	0.025
	12	50	Boiling	0.013
	9	50	Boiling	0.38
Ferric chloride	7	10	Boiling	nil
	12	10	Boiling	nil
	7	30	Boiling	nil
	9	10	Boiling	nil
Formic acid, nitrogen-sparged	9	25	35	<0.13
Formic acid	9	25	88	<0.13
	9	50	Boiling	5.08
	7	45	Boiling	nil
	12	45, 50	Boiling	nil
	7	50	Boiling	0.01
	12	90	Boiling	0.56
	7	90	Boiling	0.056

Medium	Grade	Conc'n %	Temp °C	Corr'n rate mm/yr
Hydrogen peroxide				
pH 1	7	5	23	0.062
pH 4	7	5	23	0.010
pH 1	7	5	66	0.127
pH 4	7	5	66	0.046
+500 ppm Ca ²⁺ , pH 1	7	5	66	nil
+500 ppm Ca ²⁺ , pH 1	7	20	66	0.76
Hydrogen peroxide, pH 1 + 5% NaCl	7	20	66	0.008
Magnesium chloride	7	Saturated	Boiling	nil
Methyl alcohol	9	99	Boiling	nil
Oxalic acid	7	1	Boiling	1.14
Nitric acid	9	10	Boiling	0.084
	9	30	Boiling	0.497
Phosphoric acid, naturally aerated	12	25	25	0.019
	12	30	25	0.056
	12	45	25	0.157
	12	8	52	0.02
	12	13	52	0.066
	12	15	52	0.52
	12	5	66	0.038
	12	7	66	0.15
	12	0.5	Boiling	0.071
	12	1.0	Boiling	0.14
	7	40	25	0.008
	7	60	25	0.07
	7	15	52	0.036
7	23	52	0.15	
7	8	66	0.076	
7	15	66	0.104	
7	0.5	Boiling	0.050	
7	1.0	Boiling	0.107	
7	5.0	Boiling	0.228	
Potassium hydroxide	9	50	150	9.21

Medium	Grade	Conc'n %	Temp °C	Corr'n rate mm/yr
Hydrochloric acid	9	0.5	Boiling	1.08
	9	1	88	0.009
	9	3	88	3.10
	7	5	82	0.051
	7	10	82	0.419
	9	1	Boiling	2.79
	7	0.5	Boiling	nil
	7	1.0	Boiling	0.008
	7	1.5	Boiling	0.03
	7	5.0	Boiling	0.23
	12	0.5	Boiling	nil
	12	1.0	Boiling	0.04
	12	1.5	Boiling	0.25
Hydrochloric acid, deaerated	7	3	82	0.013
Hydrochloric acid, aerated	9	5	35	0.001
	7	1,5	70	<0.03
	7	10	70	0.05
	7	15	70	0.15
Hydrochloric acid, nitrogen saturated	9	5	35	0.185
Hydrochloric acid, hydrogen saturated	7	115	25	<0.025
	7	20	25	0.102
	7	5	70	0.076
	7	10	70	0.178
	7	15	70	0.33
	7	3	190	0.025
	7	5	190	0.102
	7	10	190	8.9
Hydrochloric acid, oxygen saturated	7	3,5	190	0.127
	7	10	190	9.3
Hydrochloric acid, chlorine saturated	7	3,5	190	<0.03
	7	10	190	29.0
Hydrochloric acid + 4% FeCl ₃ + 4% MgCl ₂	7	19	82	0.49
Hydrochloric acid + 4% FeCl ₃ + 4% MgCl ₂ , chlorine saturated	7	19	82	0.46
Hydrochloric acid				
+5 g/L FeCl ₃	7	10	Boiling	0.279
+16 g/L FeCl ₃	7	10	Boiling	0.076
+16 g/L CuCl ₂	7	10	Boiling	0.127
+2 g/L FeCl ₃	12	4.2	91	0.058
+0.2% FeCl ₃	9	1	Boiling	0.005
+0.2% FeCl ₃	9	5	Boiling	0.033
+0.2% FeCl ₃	9	10	Boiling	0.305
+0.1% FeCl ₃	9	5	Boiling	0.008
+0.1% FeCl ₃	7	5	Boiling	0.013
+0.1% FeCl ₃	12	5	Boiling	0.020
Hydrochloric acid + 18% H ₃ PO ₄ + 5% HNO ₃	7	18	77	nil

Medium	Grade	Conc'n %	Temp °C	Corr'n rate mm/yr
Seawater	9	-	Boiling	nil
Sodium chloride, pH 1	9	Saturated	93	Nil
Sodium fluoride				
pH 7	12	1	Boiling	0.001
pH 7	7	1	Boiling	0.002
Sodium hydroxide	9	50	150	0.49
Sodium sulfate, pH 1	7	10	Boiling	nil
Sulfamic acid	12	10	Boiling	11.6
	7	10	Boiling	0.37
Sulphuric acid, naturally aerated	12	9	24	0.003
	12	9.5	24	0.006
	12	10	24	0.38
	12	3.5	52	0.013
	12	3.75	52	1.73
	12	2.75	66	0.015
	12	3.0	66	1.65
	12	0.75	Boiling	0.003
	12	1.0	Boiling	0.91
	7	1.0	204	0.005
	7	2.0	204	nil
12	1.0	204	0.91	
Sulphuric acid, aerated	9	5	35	0.025
	7	10	70	0.10
	7	40	70	0.94
	7	5	70	0.15
Sulphuric acid, nitrogen saturated	7	10	70	0.25
	7	1,5	190	0.13
	7	10	190	1.50
	7	10	25	0.025
	7	40	25	0.23
	9	5	35	0.405
Sulphuric acid, oxygen saturated	7	110	190	0.13
Sulphuric acid, chlorine saturated	7	10	190	0.051
	7	20	190	0.38
Sulphuric acid + 5 g/L Fe ₂ (SO ₄) ₃	7	10	Boiling	0.178
Sulphuric acid + 16 g/L Fe ₂ (SO ₄) ₃	7	10	Boiling	<0.03
Sulphuric acid + 16 g/L Fe ₂ (SO ₄) ₃	7	20	Boiling	0.15
Sulphuric acid + 15% CuSO ₄	7	15	Boiling	0.64
Sulphuric acid + 1% CuSO ₄	7	30	Boiling	1.75
Sulphuric acid + 100 ppm Cu ⁺ + 1% thiourea (deaerated)	7	1	100	nil
Sulphuric acid + 100 ppm Cu ⁺ + 1% thiourea (deaerated)	12	1	100	0.23
Sulphuric acid + 1000 ppm Cl	7	15	49	0.015