Ruthenium Enhanced Titanium Alloys

MINOR RUTHENIUM ADDITIONS PRODUCE COST EFFECTIVE CORROSION RESISTANT COMMERCIAL TITANIUM ALLOYS

By R. W. Schutz

RMI Titanium Company, Niles, Ohio, U.S.A.

Several new, more highly corrosion resistant titanium alloys containing a nominal 0.1 weight per cent of ruthenium have been developed and evaluated for industrial service in corrosive environments. These improved ruthenium-enhanced α, α-β and β titanium alloys are lower in cost than the corresponding palladium-containing titanium alloys, and offer essentially the same corrosion performance in dilute reducing acids and hot brine environments. The titanium-0.1 ruthenium binary alloys can be cost effectively substituted for traditional titanium-palladium alloys and should represent a more attractive alternative to nickel-chromium-molybdenum alloys in hot, acidic brine applications. The corrosion database that has been established for the higher strength ruthenium-enhanced α-β and β titanium alloys in high temperature sweet and sour brines provides the basis for their selection for applications in the chemical process, oil/gas production, offshore and geothermal energy industries.

Traditionally, the palladium-containing titanium alloys, ASTM (American Society for Testing and Materials) Grades 7 and 11 titanium (titanium-0.15 weight per cent palladium, Ti-0.15Pd) have been the most corrosion resistant titanium alloys commercially available. These titanium-palladium, Ti-Pd, alloys were selected when other common industrial titanium alloys, such as the unalloyed grades, exhibited susceptibility to crevice and pitting corrosion in more aggressive chemical service. Severe service environments include chlorine-saturated brines, wet halogens, acidic metal chloride solutions (such as $FeCl_3$, $ZnCl_2$, $AlCl_3$) and hydrolysable, concentrated brines (such as $MgCl_2$, $CaCl_2$) at temperatures exceeding ~ 80°C. The Ti-Pd alloys are also corrosion resistant over a much wider range of temperatures and/or acid concentrations in hot dilute inorganic and organic reducing acids (1).

Despite their dramatically enhanced corrosion performance, the utilisation of Grades 7 and 11 titanium alloys has been severely limited over the past thirty years due to their high relative cost. As is shown in Table I, the cost of Ti-Pd alloy is almost twice that of unalloyed titanium and is similar to that of common nickel-chromium-molybdenum, Ni-Cr-Mo, alloys on a dimensional (density-normalised) basis. The higher cost of the titanium alloy results solely from its palladium content, based on a nominal addition of 0.15 to 0.18 weight per cent (at a price taken in November 1995 of \$144/troy ounce for palladium powder).

Leaner Palladium-Titanium Alloys

Over the past five years titanium alloy producers have critically re-evaluated the minimum palladium content required in the alloy. Following a closer examination of the original corrosion data established by Stern and Wissenberg in the development of the Ti-Pd alloy (2, 3), it was recognised that significant savings could be achieved by reducing the nominal palladium content. Stern's profiles of corrosion rates in boiling hydrochloric acid, see Figure 1, clearly suggest that the beneficial effect due to palladium is optimised very quickly at

Table I

Approximate Mill Product Cost Ratio*
(Corrected for Density)

Alloy	ASTM Grade	Cost ratio
Unalloyed Ti	2	1.00
Ti-0.3Mo-0.8Ni	12	1.12
Ti-0.15Pd	7	1.90
Ti-0.05Pd	16	1.38
Ti-0.1Ru	26	1.15
Ti-3Al-2.5V	9	1.25
Ti-3Al-2.5V-0.05Pd	18	1.60
Ti-3Al-2.5V-0.1Ru	28	1.38
Ti-6Al-4V	5	1.22
Ti-6Al-4V-0.05Pd	24	1.57
Ti-6Al-4V-0.1Ru	29	1.34
Alloy C-276 (Ni-Cr-Mo)	–	1.90

* For 6.3 mm plate
Ratios are compared to the cost of unalloyed titanium
Costings are based on November 1995 figures

low levels, so that only minimal improvements in corrosion occur for alloys containing above ~ 0.03 weight per cent palladium (2, 3). This behaviour was confirmed in more recent hydrochloric acid corrosion rate profiles developed by Kitayama, Shida and colleagues (4, 5), and by the author, as shown in Figure 2 (6). As expected, dramatic improvements in alloy crevice corrosion resistance in hot chloride and other halide-rich aqueous media are also achieved at these lower palladium levels, see Figure 3 (5, 6).

Based on these studies, several new lean-palladium alloys, which are described in Table II, have been incorporated into ASTM product specifications. These alloys are allowed to contain 0.04 to 0.08 weight per cent palladium, with the nominal amount being 0.05 per cent. The resulting reductions in cost of Ti-Pd alloy mill products are significant, and are shown in Table I.

For applications where higher strength alloys are required, similar additions of palladium can be made to α-β or β titanium alloys to produce the cost effective alloys outlined in Table II. The corrosion performance of these higher strength palladium-enhanced alloys is documented elsewhere (6, 7).

Lean Ruthenium-Titanium Alloys

The on-going pursuit of lower cost industrial titanium alloys at the RMI Titanium Company has led to the development of ruthenium-enhanced titanium alloys. From the standpoint of alloy formulation cost, ruthenium represents the lowest cost platinum group metal addition on a per weight basis. The ruthenium powder price, in November 1995, was approximately $30 per troy ounce, which is a factor of four to five times lower than that of palladium powder. However, profiles of the acid corrosion rates for the titanium-ruthenium, Ti-Ru, binary alloy and for other titanium alloys suggest that at least twice as much ruthenium by weight is required to impart corrosion resistance comparable to that of titanium-0.05 weight per cent palladium, Ti-0.05Pd, see Figure 2 (6). Despite the need to double the weight of the ruthenium addition, the titanium alloy containing the nominal 0.1 weight per cent ruthenium still achieves cost savings of approximately 17 per cent compared with the Ti-0.05Pd (titanium Grade 16) alloy and approximately 40 per cent compared with the classic Ti-0.15Pd (titanium Grade 7) alloy. Comparative

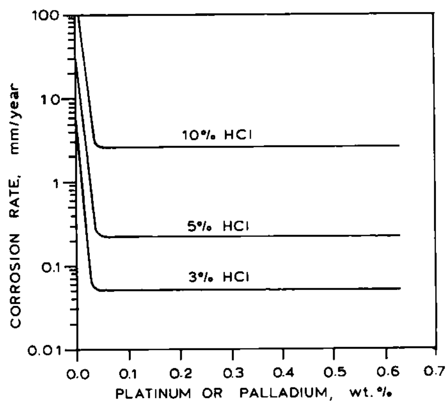

Fig. 1 Effect of the palladium content on the titanium corrosion rate in boiling hydrochloric acid solutions (2, 3)

Table II

New, Improved and Cost-Optimised Ruthenium-Enhanced Titanium Alloys for Corrosive Service

Traditional Alloy		New and Improved Alloy		Motivation for New Alloy
Alloy (UNS Number)	ASTM Grade	Alloy	ASTM Grade	New alloy
Ti-0.15Pd (R52400)	7	Ti-0.05Pd Ti-0.1Ru	16 26	Lower cost
Ti-0.15Pd* (R52250)	11	Ti-0.05Pd* Ti-0.1Ru*	17 27	Lower cost
Ti-3Al-2.5V (R56320)	9	Ti-3Al-2.5V-0.05Pd Ti-3Al-2.5V-0.1Ru	18 28	Enhanced crevice and reducing acid resistance
Ti-6Al-4V (R56400)	5	Ti-6Al-4V-0.05Pd Ti-6Al-4V-0.1Ru	24 29	Enhanced crevice, reducing acid, and SCC resistance
Ti-3Al-8V-6Cr-4Zr-4Mo (Ti-38644 or Ti Beta-C™) (R58640)	19	Ti-38644-0.05Pd Ti-38644-0.1Ru	20 –	Enhanced crevice, reducing acid, and SCC resistance

* Low interstitial/soft grade
UNS Unified Numbering System

alloy costs outlined in Table I for thin plate product suggest that ruthenium-enhanced titanium alloys offer substantial cost savings over the corresponding palladium-containing alloys.

Mechanism of Ruthenium Enhancement

The basic mechanism of ruthenium addition to titanium is considered to be very similar to that of palladium and other platinum group metals, and results from alloy ennoblement. In a similar way to palladium, ruthenium exhibits minimal solubility (less than 0.1 weight per cent) in the α-titanium phase, which results in a fine, uniform dispersion of noble Ti-Ru precipitates within the alloy (8).

When exposed to reducing acids, these precipitates, and/or ruthenium-enriched surfaces produced by selective dissolution, provide

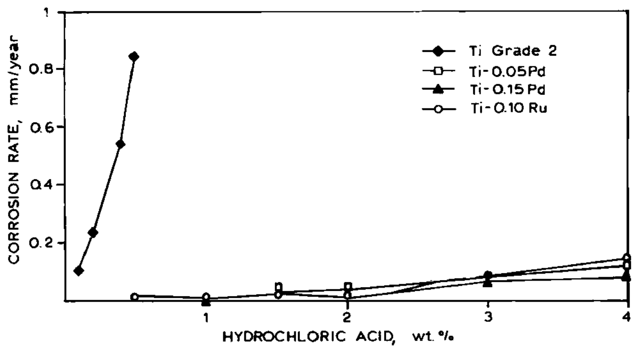

Fig. 2 Corrosion rate profiles for titanium-0.1 per cent ruthenium and titanium-palladium alloys in boiling hydrochloric acid solutions

cathodic sites of low hydrogen overvoltage and accelerated hydrogen ion (H_3O^+) reduction (9, 10). This depolarisation of the hydrogen ion reduction reaction, or "cathode-modification" phenomenon, produces a substantial shift in the corrosion potential of the titanium alloy in acid towards the noble (positive) direction where the protective surface oxide film, TiO_2, is stable (1), and full passivity can be achieved. This has been a highly effective and well-known technique for improving the corrosion performance of titanium alloy, due to the well established active-passive behaviour of titanium in reducing acids and its exceptionally high anodic pitting potential in acid solutions.

Ruthenium alloy additions also effectively inhibit titanium crevice corrosion in hot aqueous halide and sulphate environments. This enhanced crevice corrosion resistance results from the same "cathode modification" mechanism discussed above for reducing acids. With time, the solution within a tight metal crevice exposed to hot salt solutions often becomes a more aggressive deaerated reducing acid (1). This explains the dual beneficial effects from the ruthenium addition, both in reducing acid exposure and within crevices. Creviced surfaces are ennobled and local passivity is maintained within acidic crevices. The enhanced crevice resistance of Ti-Ru alloys is essentially equivalent to that of Ti-Pd alloys, as indicated by the guidelines in Figure 3.

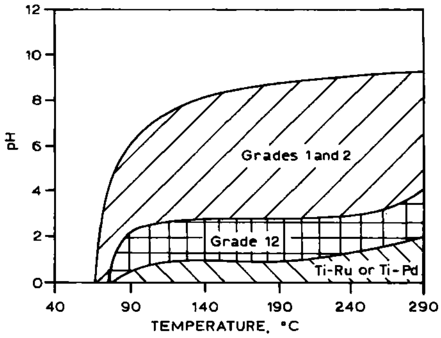

Fig. 3 Temperature-pH limits for crevice corrosion of titanium alloys in naturally-aerated sodium chloride-rich brines. (The shaded areas are regions where alloys are susceptible to attack)

Higher Strength Ruthenium-Enhanced Titanium Alloys

Greater strength in titanium is commonly achieved by the addition of alloying elements, such as aluminium and vanadium, to form

Table III

Minimum Tensile Strength Values for New Ruthenium-Enhanced Titanium Alloys

Alloy	ASTM Grade	Alloy type	Minimum Yield Stress, ksi (MPa)	Minimum Ultimate Tensile Strength, ksi (MPa)
Ti-0.15Pd	7	α	40 (275)	50 (345)
Ti-0.1Ru	26	α	40 (275)	50 (345)
Ti-0.15Pd*	11	α	25 (170)	35 (240)
Ti-0.1Ru*	27	α	25 (170)	35 (240)
Ti-3Al-2.5V	9	α-β	70 (483)	90 (620)
Ti-3Al-2.5V-0.1Ru	28	α-β	70 (483)	90 (620)
Ti-6Al-4V ELI	23	α-β	110 (759)	120 (827)
Ti-6Al-4V-0.1Ru	29	α-β	110 (759)	120 (827)

* Low interstitial/soft grade
ksi is 1000 lb/in^2
ELI is Extra Low Interstitials

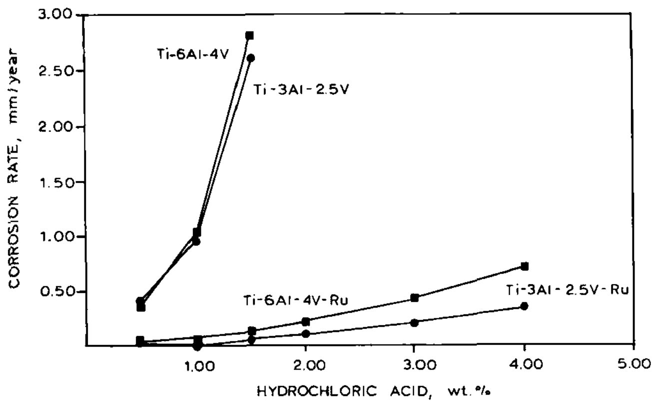

Fig. 4 Corrosion rate profiles for α-β titanium alloys in boiling hydrochloric acid solutions showing the benefits of ruthenium additions

α-β or β-phase alloys. With the exception of molybdenum, most common alloying elements, and especially aluminium, diminish the reducing acid- and hot halide crevice-corrosion resistance of titanium alloys, with increasing content (11). The titanium-3 aluminium-2.5 vanadium, Ti-3Al-2.5V, (titanium Grade 9) and titanium-6 aluminium-4 vanadium, Ti-6Al-4V, (titanium Grade 5) alloys are two such common α-β alloys which exhibit attractive medium-to-high strength properties, see Table III, but in certain environments they possess corrosion resistance inferior to that of unalloyed titanium. In fact, the Grade 9 titanium alloy was recently incorporated into the ASME (American Society of Mechanical Engineers) Pressure Vessel Code for use at temperatures up to 315°C, and offers significantly higher design allowables compared with other titanium alloys listed in the Code. Unfortunately, this alloy is susceptible to crevice corrosion in chloride- or other halide-rich service environments at temperatures above ~ 80°C (depending upon pH, etc.), thus severely limiting application and design opportunities. The higher strength titanium Grade 5 alloy also exhibits susceptibility to stress corrosion in brine and aqueous halides which similarly limits its use at increased temperatures.

The deficiencies in the corrosion performances of these high strength titanium alloys can also

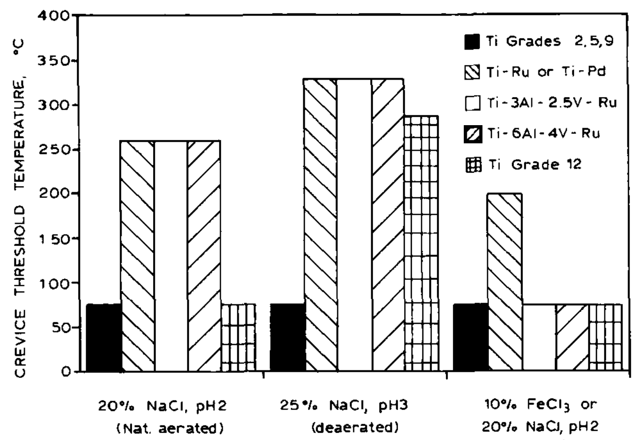

Fig. 5 Approximate temperature thresholds for crevice corrosion of ruthenium-enhanced titanium alloys in acidic chloride brines

Table IV

Results of Stress Corrosion Cracking Tests for Ruthenium-Enhanced Titanium Alloys in High Temperature Brines

Alloys tested	Test media	Types of SCC tests	Temperature of tests, °C	SCC or localised attack?
Ti-6Al-4V-Ru Ti-3Al-2.5V-Ru Ti-3Al-8V-6Cr-4Zr-4Mo-Ru	Sour gas well brine	• C-ring • Slow strain rate	260 232, 260, 288	No No
Ti-6Al-4V-Ru Ti-3Al-2.5V-Ru	Sour geothermal brine	• U-bend • C-ring • Slow strain rate	302, 330 330 302, 330	No No No
Ti-6Al-4V-Ru	Hypersaline geothermal brine	• U-bend • Slow strain rate	260 25, 260, 274	No No

Sour gas well brine: deaerated 25% NaCl, 1000 psig H_2S, 500 psig CO_2, 1 g/l S, pH 3.5

Sour geothermal brine: 20,000 ppm Cl^-, 800 ppm SO_4^{2-}, 4 ppm F^-, 12,420 ppm Na^+, 1200 ppm K^+, 20 psig H_2S, 100 psig CO_2, pH 2.3 (deaerated)

Hypersaline geothermal brine: 15.2% NaCl, 2.45% KCl, 6.7% $CaCl_2$, 200 psig CO_2, pH 4.0 (deaerated)

be effectively reduced by nominal additions of 0.1 weight per cent ruthenium. Corrosion studies performed upon ruthenium-enhanced α-β titanium alloys reveal substantial improvements in their resistance to reducing acids, hot chloride crevice corrosion and stress corrosion cracking (6). Alloy corrosion rate profiles in boiling hydrochloric acid, presented in Figure 4, show the obvious benefit of ruthenium additions. The mechanism of corrosion resistance is again the same "cathode modification" (ennoblement) and oxide film stabilisation phenomenon as discussed previously for the binary Ti-Ru and Ti-Pd alloys.

The dramatic elevation of the threshold temperatures at which crevice corrosion starts in naturally-aerated acidic brines is indicated in Figure 5 for the ruthenium-enhanced α-β alloys. This enhancement has been confirmed via "worst-case" Teflon gasket-to-metal crevice tests in sweet and highly sour concentrated brines and in deaerated hypersaline Salton Sea geothermal brines down to pH 2 (6). In more aggressive, severely-oxidising (chlorine saturated or $FeCl_3$-rich) acidic brines, the crevice resistance of these higher strength alloys may be restricted to pH values above 3, when temperatures exceed ~ 80°C.

Although the Ti-3Al-2.5V alloy is not generally susceptible to stress corrosion cracking (SCC) in aqueous media, it is known that the Ti-6Al-4V alloy can exhibit halide SCC susceptibility, especially when the aluminum and/or interstitial levels increase (12). This serious limitation can be alleviated during exposure to hot aqueous halide (brine) by ruthenium addition to the ELI (Extra Low Interstitials with a 0.13 per cent oxygen maximum) Ti-6Al-4V alloy base. The SCC test results outlined in Table IV support the selection of these modified α-β titanium alloys for use in either sweet or sour sodium chloride-rich brines at temperatures as high as 330°C. These hot brine test environments are typical of those in Salton Sea geothermal brine wells in California and in deep sour gas wells in the Gulf of Mexico.

Similar improvements in high temperature corrosion behaviour can be achieved in β-titanium alloys by the addition of ruthenium. Corrosion studies conducted by the author on the Ti-38644 (titanium Grade 19) (Ti Beta-C™) alloy suggest that the mechanism is again

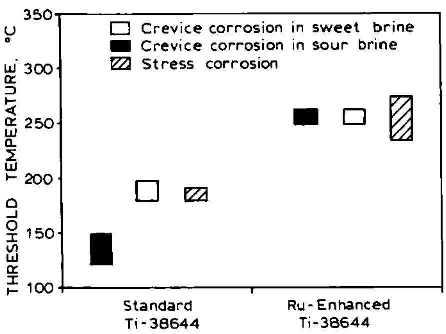

Fig. 6 Approximate temperature thresholds for crevice and stress corrosion of standard and ruthenium-enhanced Ti-38644 alloys in sweet and sour sodium chloride brines

"cathode-modification". Of particular engineering value are the dramatic increases in the threshold temperatures for crevice corrosion and SCC offered by the ruthenium-enhanced Ti-38644 alloy in sweet and sour sodium chloride-rich brines (13), see Figure 6.

Status and Potential Applications for Ruthenium-Containing Titanium Alloys

Since the minor addition of 0.1 weight per cent ruthenium to these titanium alloys has no significant influence on their mechanical and physical properties, the new ruthenium-containing alloys are specified with the same minimum tensile properties as the corresponding base alloys. Values for the minimum tensile properties required by ASTM product specifications are listed in Table III. The four new ruthenium-containing α and α-β alloys, with a permitted ruthenium content of 0.08 to 0.14 per cent, have been assigned the ASTM grade numbers indicated in Table II. They have recently been incorporated in appropriate ASTM specifications for sheet, strip and plate (B265), forgings (B381), bar and billet (B348), seamless and welded pipe (B337, B861 and B862), fittings (B363), tubing (B338) and wire (B863). ASTM Grades 26, 27 and 28 titanium alloys will soon be submitted for approval and eventual incorporation into the ASME Pressure Vessel Code. The ASME Code design allowables specified for these three alloys should mimic those for titanium Grades 7, 11 and 9 alloys, respectively, already in the Code.

Some other possible applications for the titanium-0.1 ruthenium alloys (Grades 26 and 27) in the chemical and process industries are listed in Table V. These alloys offer cost effective, direct replacement of titanium Grade 7 and 11 alloys. The lower cost of these Ti-Ru alloys should also result in increased use of titanium in traditional Ni-Cr-Mo alloy applications which involve dilute acids and/or halide-rich process streams.

Current candidate applications for the higher strength ruthenium-enhanced titanium alloys

Table V

Candidate Applications for Titanium-0.1 Ruthenium Alloys

Chloralkali and chlorate cell anodes, liners and components
Hot seawater/brine plate exchangers*
Hot Ca, Mg salt brines
Hot acidic metal halides ($FeCl_3$, $CuCl_2$, $AlCl_3$, $NiCl_2$ and $ZnCl_2$)
Hot aqueous Cl_2/Br_2 (wet halogens) and Cl_2-saturated brines
Hot dilute organic and inorganic acids
MnO_2 anodes
FGD (Flue Gas Desulphurisation) scrubber inlets/prescrubbers
Steel tubesheet/vessel explosive cladding*

* Requires softer, lower interstitial grades of these alloys

Table VI

Candidate Applications and Components for Ruthenium-Enhanced α-β and β Titanium Alloys

Application	Applicable Alloys		
	Ti-3Al-2.5V-Ru	Ti-6Al-4V-Ru	Ti-38644-Ru
Wet oxidation processes	X		
Other waste treatment processes	X		
High temperature organic synthesis	X		
Hydrometallurgical ore leaching processes	X	X	
Deep sour gas and geothermal well tubulars	X	X	X
Downhole tools and accessories		X	X
Offshore flowlines, export and catenary risers	X	X	
Coiled tubing	X		
Pressure vessels, heat exchangers	X		
Valves, pumps, shafting		X	
Fasteners		X	X
Agitators	X	X	
Seamless piping	X	X	X
Welded piping	X		

are outlined in Table VI. Note that the titanium Grades 28 and 29 alloys are also currently in the final stage of approval for incorporation in the NACE (National Association of Corrosion Engineers) MR-01-75 Standard for use in sour service; allowing these new alloys to be selected for many deep oil/gas wells and offshore production components.

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