Tantalum surface alloys: Next generation of corrosion protection.

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Summary
Tantalum surface alloys offer a new route to corrosion resistance in severe corrosion environments like hot concentrated acids.
The tantalum surface alloy is deposited on stainless steel substrates at 700-900℃.

Corrosion testing in wet chlorine gas at room temperature, liquid bromine at room temperature, 32% hydrochloric acid at 75℃, 85% sulphuric acid at 80℃ and glacial acetic acid at 205℃ show no corrosion of Tantaline specimens.

Thermal cycling of Tantaline specimens by water quench from 300℃ does not impair corrosion resistance and cross sections show no cracking or deterioration after 100 quench cycles.

Mechanical deformation of Tantaline specimens by Rockwell indentation and subsequent U-bending of tantalum treated stainless steel strips does not impair corrosion resistance. Cross sections of deformed strips show no cracks or delamination.

Introduction
The need for corrosion-resistant materials is continuing to grow as engineers push their existing processes harder to gain more efficient production and as new next-generation processes, which are far more demanding, come online. These processes push conventional materials and specialty alloys beyond their limits, creating a strong need for new material solutions.

The tantalum vapor surface alloying technology takes advantage of the superior corrosion resistance properties of tantalum. In a furnace heated to 700-900℃ tantalum metal is chemically deposited. The tantalum diffuses into the substrate, typically stainless steel, creating a surface alloy. The gaseous tantalum atmosphere is maintained in the furnace so that a dense layer of pure tantalum grows on the surface of the part over the diffusion layer to a thickness of 50µm.
The Tantaline treated part has its original part size and shape, but has the same chemical properties and corrosion resistance as pure tantalum metal.

The result is a product with the corrosion resistance of tantalum metal, at costs competitive with specialty alloys like Hastelloy® C276 maintaining the easy commercial availability of stainless steel products.

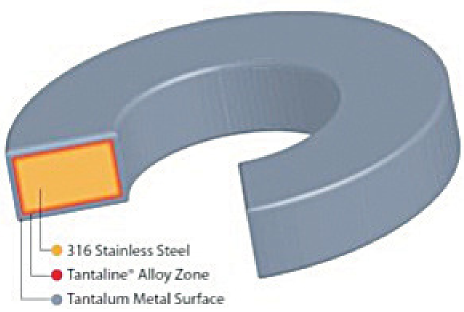

Figure 1. Schematic cross section of a treated stainless steel washer showing the surface alloy diffusion zone and pure tantalum metal surface.

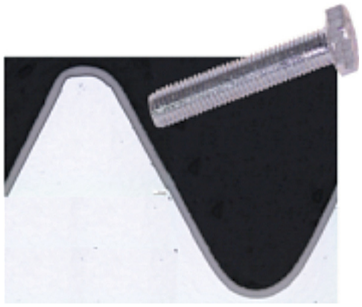

Figure 2. Micrograph showing cross section of Tantaline treated Fastener. Original profile is preserved.

Tantalum, and hence Tantaline, offers zero corrosion in many hot concentrated acid environments including hydrochloric, sulfuric, nitric and phosphoric acid, and mixtures of these up to 150℃. This makes Tantaline interesting for chemical process industry, pharmaceuticals, fine chemicals as well as sour oil and gas processing where high nickel alloys and other specialty materials are applied. Some product examples are:

- Flanged valves and thermo wells for chemical process industry
- Heat exchangers
- Compression fittings and valves for pilot plant systems
- Laboratory scale reactors
- Metal felt for catalyst support

Experimental

Specimens for all tests are tantalum treated using standard Tantaline surface alloy procedure. Tantalum thickness is 50µm.

Corrosion tests are performed in suitable heated and/or pressurized vessels. Temperature is monitored using calibrated thermocouple. Test specimens are fully submerged.

Mechanical ruggedness specimens were indented with a Rockwell C cone indenter at the midpoint and subsequently U-bent 180° over a 3/8" (10mm) mandrel stretching the indented area. After bending the specimens are corrosion tested in boiling 37% hydrochloric acid for 24 hours. Finally specimens are sectioned and cross sections inspected.[1]

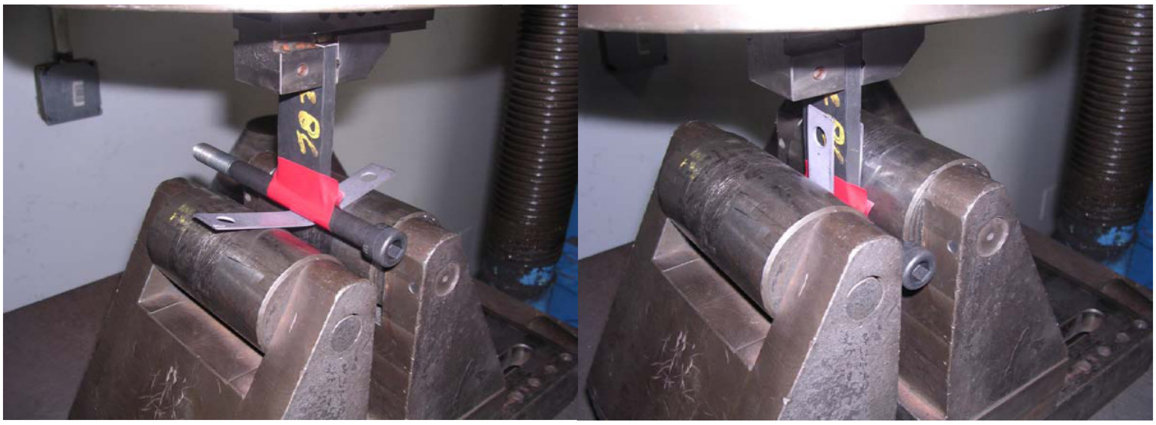

Figure 3. U-bending over 3/8" mandrel. Rockwell identations are at centre of strip on lower side experiencing tensile deformation.[1]

Thermal cycling specimens are heated in a horizontal furnace to 300℃. Temperature is measured with calibrated thermocouple placed inside specimen cavity. When temperature is reached specimen is pulled out and immediately (within 5 seconds) quenched in water. Quench cycle is repeated 100 times.
After 100 cycles the specimens are corrosion tested in 32% hydrochloric acid at 75℃ for 48 hours. Finally specimens are sectioned and cross sections inspected.

Test results
Corrosion testing in hot hydrochloric acid and hot sulfuric acid, has verified that the tantalum treated parts show no corrosion after 1 month as expected for tantalum. Reference samples of high nickel alloys, titanium and stainless steels all had severe corrosion attacks. Corrosion rate is calculated from weight loss.

Table 1: Corrosion rates (weight loss) for Tantaline and other corrosion resistant materials in hot mineral acids.

Corrosion (mm/yr)	Tantaline	C-276	Alloy 20	Inconel 625	Titanium	CM-400	Duplex 2205
32% HCl 75℃	<0.001	0.7	>10	>10	>10	>10	>10
85% H_2SO_4 80℃	<0.001	0.2	0.3	1	>10	1	0.5

Corrosion testing in glacial acetic acid has verified that tantalum treated parts show no corrosion after 6 weeks. Solid tantalum reference show no corrosion while zirconium reference showed slight corrosion.

Table 2: Corrosion rates (weight loss) for Tantaline, solid tantalum and zirconium in glacial acetic acid.[2]

Corrosion (mm/yr)	Tantaline	Tantalum-190D	Zirconium 705
Glacial Acetic Acid at 205℃ (14 bar)	<0.0005	<0.0005	0.003

Corrosion testing in wet chlorine gas and liquid bromine at room temperature verifies tantalum treated parts showing no corrosion as expected for tantalum. Fluorinated polymer coatings and nickel plating suffer various degree of attack. Stainless steel references are corroded by both chlorine and bromine.

Table 3: Corrosion testing of Tantaline and various coating systems at ambient temperature for 1 month.[2]

	Tantaline	FEP (Fluorinated Polymer)	Nickel Plating	Xylan (Fluorinated Polymer)	Stainless Steel (reference)
Wet Chlorine Gas	No Corrosion	Disbonded coating. Severe corrosion	Plating completely dissolved. Severe corr.	Disbonded coating. Severe corrosion	Severe corrosion
Liquid Bromine 99.8%	No Corrosion	Delaminated coating. Corrosion	Traces of plating remain. Severe pitting	Blistering of coating	Corrosion

The mechanical ruggedness of the surface alloy was tested. Samples were indented with a Rockwell C cone indenter at the midpoint and U-bent 180° over a mandrel before testing in boiling 37% hydrochloric acid for 24 hours. All the samples survived with no signs of corrosion.[1]

Figure 5: Ruggedness test coupon indented with Rockwell C and U-bent over 3/8” (10mm) mandrel. [1]

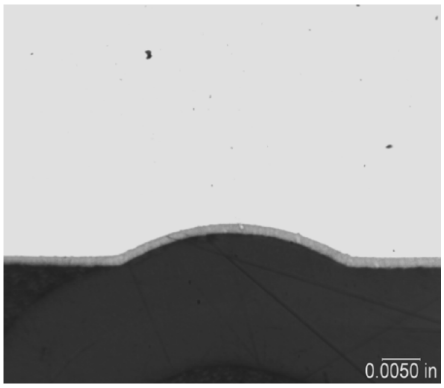

Figure 6: Micrograph showing uniform deformation of substrate and tantalum surface alloy at indentation. No cracks or delamination is seen. [1]

Thermal cycling between 300℃ and room temperature, cooling by water quench, has demonstrated good resistance to thermal shock. After 100 quench cycles still no corrosion was seen in 32% hydrochloric acid at 75℃ for 48 hours and metallographic sectioning showed no cracks or other signs of deterioration.

Figure 4: Cross section of thermal shock test specimen. After 100 water quench cycles from 300℃ no crack or signs of deterioration is seen.

Conclusion

The tantalum surface alloy has zero corrosion in wet chlorine gas, liquid bromine as well as hot hydrochloric, sulfuric and acetic acids during the test period as expected for tantalum. This verifies that the tantalum layer is dense and fully covering the underlying stainless steel substrate.

Severe mechanical deformation and thermal cycling does not impair the corrosion resistance. This verifies that the surface alloy that is formed provides an extremely strong bond between tantalum and the stainless steel. The surface alloy makes Tantaline products extremely rugged and durable compared to typical coatings where bonding is primarily mechanical.

References

[1] Hira Ahluwalia, unpublished report.

[2] Corrosion Testing Laboratories Inc. , unpublished report