# Tantalum Materials in the CPI for the Next Millennium

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#### ABSTRACT

Tantalum materials have been used in the Chemical Processing Industry (CPI) for over 60 years and continue to be important materials of construction. This paper will discuss tantalum and Ta-2.5W alloy applications that have evolved over the past century to current day applications. Traditional upper limits for corrosion and hydrogen embrittlement resistance established for pure tantalum will be compared to new upper limits for the Ta-2.5W alloy in HCl, NaOH and H<sub>2</sub>SO<sub>4</sub> acid media. Also illustrated, will be test data showing the pronounce affect of coupling platinum to tantalum materials, and their contributions on establishing new upper boundaries for tantalum materials for the CPI.

#### **INTRODUCTION**

A significant amount of research and development by several chemical companies was carried out in the latter half of the 1950's to determine the suitability of pure tantalum (UNS # R05200) for handling hot concentrated chemical compounds where most other metals and non-metallic materials were not suitable<sup>1</sup>. Some of the largest and most important improvements, since the first equipment installations in the early 1930's, have been the improvements in fabrication and inspection techniques to minimize the overall amount of tantalum required to fabricate lined vessels, piping and heat exchangers. Further improvements were made in the early 60's by alloying tantalum with tungsten to improve mechanical strength by 30% as well as increasing corrosion resistance without degrading the other physical properties of pure tantalum. Thinner cross sections were used to optimize the designs, minimizing the overall amount of tantalum material required fabricating CPI processing equipment. After several years of chemical plant performance and production of the tantalum-tungsten mill products, the tantalum-tungsten alloy (UNS # R05252) was established with a tungsten range of 2.0 to 3.5 wt %. Since the

introduction and commercialization of the Ta-2.5W alloy, a limited amount of corrosion resistance testing has been published, however plant performance of the Ta-2.5W alloy has lead to the replacement of UNS # R05200 tantalum for the majority of CPI processing equipment applications.

Hydrogen embrittlement is one of the primary concerns when dealing with reactive metals, such as tantalum, in severe acid service. For tantalum and tantalum alloys, significant embrittle begin to occur at hydrogen concentrations greater than 100 ppm (Nitrogen and oxygen begin to significantly embrittle tantalum at concentrations greater than 1000 ppm). On the other hand, this high reactivity also leads to the formation of extremely stable oxides that are a necessary prerequisite for excellent corrosion resistance to concentrated acids. The thin protective oxide layer on tantalum, Ta<sub>2</sub>O<sub>5</sub>, strongly bonds to the metal, is essentially free of defects, and reforms spontaneously in case of damage.

At temperatures in the range of approximately 190°C to 250°C, however, the protective  $Ta_2O_5$  oxide film changes depending on the environment involved. The oxide begins to break down, degrading the interfacial bond with the metal. Consequently, the corrosion resistance and inertness of tantalum begins to degrade and chemical attack becomes extensive and rapid. In the presence of hydrogen containing acids and/or when in contact with metals that are more electronegative, tantalum can become hydrogen embrittled as a result of diffusion of atomic hydrogen along tantalum grain boundaries<sup>1</sup>.

This paper will address corrosion and hydrogen embrittlement of tantalum and Ta-2.5W alloy in the presence of sulfuric acid as well as hydrochloric acid and sodium hydroxide solutions at elevated temperatures. This particular work extends the corrosion knowledge of these materials from an extensive study performed and presented by Dr. Renner of Bayer Corp. materials department in 1997.

## **EXPERIMENTAL PROCEDURE**

A corrosion test matrix was developed to determine the propensity of hydrogen embrittlement and corrosion resistance of tantalum and Ta-2.5W alloy to various acids and bases. H.C. Starck provided all the test specimens. A weld bead was run lengthwise down the center and on both sides of each specimen. Half of each of the tantalum and Ta-2.5W samples were platinum spotted at SIFCo Selective Plating. The tantalum test samples were identified as follows:

- 1. Ta Pure Tantalum
- 2. Ta/Pt Pure Tantalum with Platinum Spot
- 3. TaW Ta-2.5%W Alloy
- 4. TaW/Pt Ta-2.5%W Alloy with Platinum Spot

Corrosion Testing Laboratories (CTL) performed all the corrosion tests. The test specimens, measuring approximately 25 mm by 38 mm by 0.5 mm thick, were cleaned, weighed, and measured prior to testing. Individual test specimens were fully immersed in each solution (environment) listed in Table I. The samples were separated from each other using Teflon spacers. For the tests performed in  $H_2SO_4$  acid, samples were also removed from testing after 8 weeks.

All of the tests, except for the tests in HCl acid, were performed in conventional plastic labware. The HCl acid tests were performed in specialized, Teflon-lined pressure vessels. For environment #5, copper was added using CuCl<sub>2</sub>. After the test cycle was completed, each sample was rinse and dried. Corrosion rate evaluations were performed based on weight change. Localized corrosive attack was evaluated by visual examination at 20x. The corrosion rate (mils/yr) was calculated based on the weigh change data.

<b>CORROSION TEST ENVIRONMENTS</b>							
Test No.	Acid Composition	Temperature	Duration				
1	5% NaOH	100°C	28 days				
2	10% NaOH	38°C	28 days				
3	10% NaOH	66°C	28 days				
4	10% NaOH	100°C	28 days				
5	18% HCl + 200 ppm Cu	220°C	28 days				
6	30% HCl	200°C	28 days				
7	96% H <sub>2</sub> SO <sub>4</sub>	230°C	15 weeks				
8	97% H <sub>2</sub> SO <sub>4</sub>	230°C	15 weeks				
9	97.5% H <sub>2</sub> SO <sub>4</sub>	230°C	15 weeks				
10	97.9% H <sub>2</sub> SO <sub>4</sub>	230°C	15 weeks				

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# **RESULTS & DISCUSSION**

Figures 1 to 11 and Table II show the results of the corrosion tests in the various acids listed in Table I. A summary of the test results for each acid is presented below. Samples were removed from testing if severe corrosive attack was observed after 3 days for tests #1 to #6 and 8 weeks for tests #7 to #10.

				8 wk	15 wk
Test		Test	Corrosion	Н	Н
No.	Acid Composition/Temp(°C)/Duration	Sample	Rate (mils/yr)	(ppm)	(ppm)
1	5% NaOH / 100°C / 4 weeks	Та	7.4		993
		Ta/Pt	8.3		288
		TaW	7.5		1513
		TaW/Pt	8.4		203
2	10% NaOH / 38°C / 4 weeks	Та	0.7		2
		Ta/Pt	1.4		2
		TaW	1.0		139
		TaW/Pt	3.1		234
3	10% NaOH / 66°C / 4 weeks	Та	8.3		792
		Ta/Pt	9.0		752
		TaW	15.9		2276
		TaW/Pt	15.8		2275
4	10% NaOH / 100°C / 4 weeks	Та	7.9		6
		Ta/Pt	11.1		6
		TaW	19.2		258
		TaW/Pt	18.8		613
5	18% HCl + 200 ppm Cu / 200°C / 4 weeks	Та	0.1		5
		Ta/Pt	0.1		3
		TaW	0.1		2
		TaW/Pt	0.1		1
6	30% HCl / 200°C / 4 weeks	Та	1.3		8
		Ta/Pt	1.6		3
		TaW	2.9		4
		TaW/Pt	2.2		6
7	96% H <sub>2</sub> SO <sub>4</sub> / 230°C / 15 weeks	Та	4.6	201	131
		Ta/Pt	2.3	1	
		TaW	2.2	5	25
		TaW/Pt	2.0	3	37
8	97% H <sub>2</sub> SO <sub>4</sub> / 230°C / 15 weeks	Та	4.6	154	122
		Ta/Pt	2.9	1	164
		TaW	2.3	5	35
		TaW/Pt	2.2	1	13
9	97.5% H <sub>2</sub> SO <sub>4</sub> / 230°C / 15 weeks	Та	5.7	138	265
		Ta/Pt	3.0	1	202
		TaW	2.5	4	19
		TaW/Pt	1.7	3	9
10	97.9% H <sub>2</sub> SO <sub>4</sub> / 230°C / 15 weeks	Та	6.9	143	169
		Ta/Pt	2.3	1	82
		TaW	2.0	2	15
		TaW/Pt	1.7	1	18

TABLE IICORROSION RATES FOR TANTALUM AND Ta-2.5W SAMPLES\*

\* Initial hydrogen concentrations in Ta and Ta-2.5W were <2 ppm

### **NaOH Environments**

A visual evaluation of the samples tested in 5% NaOH showed pitting type attack that was heaviest away from the weld and HAZ, Figure 1. For the Ta sample, there was also a translucent white deposit in the pits. For the Ta and TaW samples, the pits were deeper than on the Ta/Pt and TaW/Pt samples. There were also areas of heavy, non-uniform attack where Teflon spacers were placed between the samples. Approximately 75% of the platinum spots were still visible on the Ta/Pt and TaW/Pt samples.

All the samples tested in the 10% NaOH at 38°C showed almost negligible attack except where the Teflon spacers were in contact with the sample, Figure 2. For the TaW and TaW/Pt samples, there was also some light general corrosive attack away from the weld and HAZ. These latter areas showed no corrosive attack. On the Ta/Pt and TaW/Pt samples, approximately 100% and 20% of the platinum spots were still visible, respectively.

All the samples tested in the 10% NaOH at 66°C showed general uniform corrosive attack and slightly greater attack where the Teflon spacers were in contact with the sample, Figure 3. Also, the TaW and TaW/Pt samples showed greater attack than the Ta and Ta/Pt samples, respectively. Both the TaW and TaW/Pt samples cracked during cleaning. On the Ta/Pt and TaW/Pt samples, the platinum spots were completely removed. The results for the samples tested in the 10% NaOH at 100°C were exactly the same as described above, Figure 4, although the general uniform corrosive attack was heavier than on the samples tested at 66°C. There was also some pitting of the Ta and Ta/Pt samples were the Teflon spacers were in contact with the samples.



FIGURE 1 – 5% NaOH at 100°C, Ta, Ta/Pt, TaW, and TaW/Pt samples, respectively.



FIGURE 2 – 10% NaOH at 38°C, Ta, Ta/Pt, TaW, and TaW/Pt samples, respectively.



FIGURE 3 – 10% NaOH at 66°C, Ta, Ta/Pt, TaW, and TaW/Pt samples, respectively.

For the 5% NaOH solution, the corrosion rate on all the samples similar. While platinum spotting marginally improved the corrosion resistance of tantalum and Ta-2.5W alloy, higher hydrogen enrichment (and embrittlement) was greatly reduced. For the 10% NaOH solutions, the corrosion rate on the TaW and TaW/Pt samples was greater than on the Ta and Ta/Pt samples. Platinum spotting did not significantly improve the corrosion resistance for either tantalum or the Ta-2.5W alloy. This increased corrosive attack also produces significantly higher hydrogen enrichment (and embrittlement) in the TaW and TaW/Pt samples. As will be seen later in this paper, platinum spotting almost always improves the corrosion resistance of both the pure tantalum and the Ta-2.5W alloy. However, this is not the case when pure tantalum and the Ta-2.5W alloy are exposed to NaOH.

# **HCl Environments**

All the samples tested in the 18% HCl + 200 ppm Cu at 220°C showed no visible signs of corrosive attack except for some very light etching on the Ta/Pt sample, Figure 5. On the Ta/Pt and TaW/Pt samples, the platinum spots were completely removed. Hydrogen enrichment was almost non-existent in all the samples.

All the samples tested in the 30% HCl at 200°C showed some very light general uniform corrosive attack, Figure 6. Surprisingly, the TaW and TaW/Pt samples showed slightly greater corrosion rates than the Ta and Ta/Pt samples, respectively. On the Ta/Pt and TaW/Pt samples, approximately 85% and 65% of the platinum spots were still visible, respectively. Hydrogen enrichment was almost none existent in all the samples.



FIGURE 4 – 10% NaOH at 100°C, Ta, Ta/Pt, TaW, and TaW/Pt samples, respectively.



FIGURE 5 – 18% HCl + 18 ppm Cu at 220°C, Ta, Ta/Pt, TaW, and TaW/Pt samples, respectively.



FIGURE 6 – 30% HCl at 200°C, Ta, Ta/Pt, TaW, and TaW/Pt samples, respectively.

#### H<sub>2</sub>SO<sub>4</sub> Environments

A visual evaluation of the samples tested in  $H_2SO_4$  acid showed little evidence of chemical attack with the exception of some light etching of the weld and weld HAZ, Figures 7 to 10. However, the platinum spots were completely dissolved/removed from the Ta/Pt and TaW/Pt samples after eight weeks of testing although there was evidence the spot had been present on the samples at the start of the corrosion test. After eight weeks of exposure, all test specimens, except the Ta/Pt specimens in 97.9% acid, were coated with a loosely adherent layer of white deposits. The four Ta/Pt spot specimens exposed to the 97.9% acid did not contain any whites deposits. Instead, they were coated with a very thin, tightly adherent, light brown colored film.



FIGURE 7 – 96% H<sub>2</sub>SO<sub>4</sub> at 230°C, Ta, Ta/Pt, TaW, and TaW/Pt samples, respectively.



FIGURE 8 – 97% H<sub>2</sub>SO<sub>4</sub> at 230°C, Ta, Ta/Pt, TaW, and TaW/Pt samples, respectively.

After fifteen weeks of exposure and similar to the samples exposed for 8 weeks, all of the test specimens were coated with a loosely adherent layer of white deposits. This layer was easily removed with light brushing. No brown film was observed on any of the specimens. All of the Ta test specimens exhibited general corrosion with occasional small areas of protected metal, primarily where the Teflon spacers were in contact with the sample. The entire surface had an etched appearance, including the weld metal and the heat affected zone (HAZ). The Ta/Pt test specimens exhibited general corrosion with occasional small areas of protected metal primarily where the Teflon spacers were in contact with the sample. The entire surface had an etched appearance, including the weld metal and the HAZ. Further delamination of the Pt spots occurred in the second test period. The TaW test specimens exhibited general corrosion with occasional small areas of protected metal, primarily where the Teflon spacers were in contact with the sample and a general loss of luster on one side. Light etching was present in the weld metal and in the HAZ. Lastly, the TaW/Pt test specimens exhibited general corrosion with occasional small areas of protected metal, primarily where the Teflon spacers were in contact with the sample and a general loss of luster on one side. Light etching was present in the weld metal and in the HAZ. Lastly, the TaW/Pt test specimens exhibited general corrosion with occasional small areas of protected metal, primarily where the Teflon spacers were in contact were in contact were in the weld metal and in the HAZ.

contact with the sample and a general loss of luster on one side. Little or no etching was visible in the weld or the HAZ. Further de-lamination of the Pt spots occurred in the second test period.

The results of the chemical analysis are shown in Table II. This data shows the Ta-2.5W alloy absorbed much less hydrogen than did tantalum at all acid concentrations, with or without the platinum spot. Platinum spotting had almost no effect on the hydrogen enrichment of the Ta-2.5W alloy samples. These results are most likely due to a combination of the superior corrosion resistance of the Ta-2.5W alloy and dissolution/removal of the platinum spots. The superior corrosion resistance of the Ta-2.5W alloy results from the effect of the additional outer valence electron in tungsten helping to reduce the number of oxygen vacancies in the Ta2O5 oxide layer<sup>1</sup>. The platinum spots cathodically protect tantalum and tantalum alloys. Dissolving/removing these platinum spots removes the cathodic protection. On samples that had been platinum spotted, this would lead to the increase in hydrogen absorption seen in the samples at the fifteen week point of the test.



FIGURE 9 – 97.5% H<sub>2</sub>SO<sub>4</sub> at 230°C, Ta, Ta/Pt, TaW, and TaW/Pt samples, respectively.



FIGURE 10 – 97.9% H<sub>2</sub>SO<sub>4</sub> at 230°C, Ta, Ta/Pt, TaW, and TaW/Pt samples, respectively.

Figure 11 shows corrosion rate results for in  $H_2SO_4$  acid. These results suggest that while platinum spotting improves the corrosion resistance of pure tantalum to  $H_2SO_4$  acid, this effect can diminish over time as the platinum spot is dissolved. In the short term, platinum spotting of tantalum produces corrosion rates comparable to the Ta-2.5W alloy. For the Ta-2.5W alloy, platinum spotting also improves corrosion resistance to  $H_2SO_4$  acid; however, this effect is not as pronounced as with pure tantalum; however, when working with a tube wall thickness around .015" any improvement is significant in the overall life of the tubing. Many of the existing thermo-wells in CPI service are fabricated from pure tantalum, which would benefit from the addition of platinum spots to improve their service life. Asahi Chemicals has shown how pure tantalum instrumentation equipment which had been

embrittled in service, were recovered by vacuum annealing to remove the hydrogen<sup>2</sup>. Before placing the equipment back into service, this type of equipment would greatly benefit from the addition of a platinum spot to improve the overall life of the equipment. Additionally, as the platinum spot is dissolved, the beneficial effect of the spot is not diminishing over to the extent that this occurs in pure tantalum. The improvement in corrosion resistance with the platinum spot present is the result of the cathodic protection produced by the platinum spot.

### **CONCLUSIONS**

The results presented above show a high corrosion rate of pure tantalum and Ta-2.5W alloy in NaOH environments. These high corrosion rates are also associated with significant hydrogen enrichment and embrittlement. The exact cause for the high corrosion rate is unclear at this time. The corrosion rate for pure tantalum and the Ta-2.5W alloy in the presence of HCl is very low as is the level of hydrogen enrichment. For the level of hydrogen in these samples, embrittlement is not expected. Lastly, in  $H_2SO_4$  acid, the corrosion rate and hydrogen enrichment of the Ta-2.5W alloy is lower than for pure tantalum. Platinum spotting improves the corrosion resistance of both materials although the effect is not as great for the Ta-2.5W alloy. Additionally, dissolution of the platinum spot has little effect on either the corrosion rate of hydrogen enrichment for the Ta-2.5W alloy. The opposite is true for pure tantalum especially in regards to the corrosion rate.

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FIGURE 11 - Corrosion Rates in H<sub>2</sub>SO<sub>4</sub> Acid