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U. S. Bureau of Mines
Metals Corrosion Laboratory
College Park, Maryland

# Corrosion Studies on Titanium and Zirconium Metals

## Quarterly Report for October - December 1953

U. S. Bureau of Mines
Metals Corrosion Laboratory
College Park, Maryland

# Chemical Corrosion Studies on Titanium and Zirconium Metals

L. B. Golden, W. L. Acherman, and W. Mace

## Quarterly Report for October - December 1953

In the present reporting period a study was made on the stress corrosion cracking of spot welded titanium in red fuming nitric acid at room temperature. In earlier tests a series of ten spot welded samples prepared from 20 percent cold rolled metal (Titanium Metals Corporation designation Ti-75A) had cracked around the perimeter of the electrode indentation after thirty days exposure to the acid. The average corrosion rate was 1.93 mils per year and shear strength values were only about one-third those of the control samples (530 pounds as compared to 1640). Because of this unexpected behavior the test was repeated using a series of ten samples annealed after spot welding and another ten samples without annealing. After thirty days none of the samples in either set showed any signs of cracking and no loss in shear strength. Corrosion rates were low for both sets, 0.03 m.p.y. for the annealed samples and 0.13 m.p.y. for the others. Since conditions were apparently the same in both series of tests (i.e. metal source and welding conditions) it is not known why one series cracked so badly while another was apparently immune.

The test was again repeated using ten spot welded Ti-75A titanium samples which had been 20 percent cold rolled before welding and with no subsequent annealing. After the thirty day test shear strength values could not be obtained since the samples broke in the base metal well away from the spot weld area. All of the samples showed general embrittlement and could be broken easily by hand. Figure 1 shows a cross section of a spot weld in this series showing the general embrittlement away from the weld area and the stress corrosion cracking around the periphery of the electrode indentation. The weld nugget itself is sound, showing no signs of attack by the acid. Figure 2 shows that the embrittlement was caused by intergranular corrosion of the metal. This embrittlement was present over the entire surface of the sample and was not confined to the area near the spot weld. The average corrosion rate was 6.02 m.p.y., much higher than in previous tests. This test was made in tightly-stoppered flasks thus preventing the escape of oxides of nitrogen. The previous tests were made in loosely covered flasks allowing the gradual but continuous escape of such gases. This may account for the severity of the action of the red fuming nitric acid in the latter test but does not explain the cracking around the welds in one of the earlier tests. It is possible that the amount of cold rolling which the metal receives before spot welding may have a definite effect on the susceptibility of titanium to embrittlement and stress corrosion cracking. In order to investigate this possibility a series of spot welded samples prepared from metal which has been 0, 10, 20, 30, 40, and 50 percent cold rolled are being evaluated in red fuming nitric acid.

Further information was obtained on the effect of the addition of small amounts of corrosion inhibitors on the corrosion resistance of titanium. It was found that vanadium in the form of ammonium vanadate was a very effective inhibitor. As little as 0.0025 percent vanadium added to 40 percent sulfuric acid reduced the corrosion of titanium at 35°C in this solution from 316 to 0.27 m.p.y. (Table I). Additional amounts of vanadium reduced the corrosion rate even further (e.g. with 1 percent vanadium present the rate was only 0.09 m.p.y.). This element was equally effective in hydrochloric acid. As little as 0.0025 percent vanadium added to 20 percent hydrochloric acid at 35°C reduced corrosion from 137 to 0.42 m.p.y. Here again, increasing amounts of vanadium were even more effective since with 1 percent vanadium present the rate was only 0.08 m.p.y. Vanadium is also effective in reducing the corrosion of titanium in phosphoric and oxalic acid solutions. In these solutions however, slightly larger additions of vanadium are required in order to obtain inhibitors comparable to that in the sulfuric and hydrochloric acid solutions. In 50 percent phosphoric acid at 60°C the corrosion rate for titanium is 146 mils per year. When 1 percent vanadium is added the rate drops to 0.89 m.p.y. A similar situation exists for titanium in 5 percent oxalic acid at 60°C. Here the rate for the metal is 153 m.p.y.; addition of 1 percent vanadium reduces the rate to 0.59 m.p.y.

A study was made on the part which cupric and ferric ions play in accelerating the corrosion of high purity arc melted zirconium in sulfuric and phosphoric acid solutions. The corrosion rate for zirconium in boiling 70 percent sulfuric acid is only 0.56 m.p.y. but when 0.1 percent copper (as copper sulfate) is added the rate jumps to 420 m.p.y. Likewise, the rate in boiling 75 percent sulfuric acid is a moderate 46.2 m.p.y. but when as little as 0.05 percent copper is added the zirconium completely disintegrates in less than 24 hours. With the addition of only 0.005 percent copper the zirconium lasts for less than three days before becoming completely embrittled. The accelerating effect of copper on the corrosion of zirconium is not nearly as severe in phosphoric acid. The rate in boiling 75 percent phosphoric acid is 179 m.p.y. This is increased to 246 m.p.y. by the addition of 0.1 percent copper to the acid. Ferric ion is not nearly as effective as cupric ion in increasing the corrosion of zirconium. The corrosion rate for zirconium in boiling 75 percent sulfuric acid is 46.2 m.p.y.; the addition of 0.1 percent iron only raises this rate to 54.9 m.p.y. The effect of ferric ion in boiling 75 percent phosphoric acid was almost identical to that of cupric ion. The addition of 0.1 percent iron gave a rate of 241 m.p.y.

Samples of five high purity arc melted zirconium-carbon alloys having carbon contents of 0.008, 0.07, 0.11, 0.17, and 0.29 percent were subjected to an atmosphere of water saturated chlorine to determine the part which carbon plays on the resistance of zirconium to corrosion by this gas. Corrosion rates for a three week test at room temperature were with one exception, proportional to carbon content but were surprisingly low (0.49, 1.40, 1.54, 0.95, and 3.37 m.p.y., respectively). This test will be repeated substituting ordinary purity alloys since it now appears that possibly hafnium, and not carbon, was responsible for the poor corrosion resistance of certain lots of zirconium previously tested.

Samples of arc melted titanium and zirconium and tantalum metal were exposed for two weeks in concentrated ammonium hydroxide solution (28 percent ammonia). The test was carried out in pressure vessels at the equilibrium pressures developed at 60° and 100°C. None of these metals showed any signs of attack and corrosion rates were all zero except for titanium at 100°C with a rate of only 0.03 m.p.y. The test was also run using solid ammonium carbonate with no visible signs of attack resulting and zero corrosion rates for all the metals.

Future program: The program for the immediate future will include further studies on the stress corrosion cracking of spot welded titanium in red fuming nitric acid with metal which has received increasing amounts of cold rolling before welding. Titanium heliarc welds will be evaluated in selective corrosive media to determine the effect of contaminated atmospheres during the welding process on the corrosion resistance of the resultant welds. Further information will be obtained on the effect of the addition of small amounts of corrosion inhibitors on the corrosion resistance of titanium.

Table I. Effect of Vanadium Ion on the Corrosion Resistance of of Titanium in Various Acid Solutions

| Acid concentration (percent by wgt.) | Temp. °C | Average corrosion rate, 6-day run, mils per year | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | Percent vanadium ion added[1/] | | | | | | | | |
| | | 0.00 | 0.0025 | 0.005 | 0.01 | 0.05 | 0.1 | 0.25 | 0.50 | 1.0 |
| 40 $H_2SO_4$ | 35 | 316 | 0.27 | 0.25 | 0.17 | 0.12 | 0.13 | 0.13 | 0.12 | 0.09 |
| 20 HCl | 35 | 137 | 0.42 | 0.26 | 0.20 | 0.13 | 0.09 | 0.14 | 0.12 | 0.08 |
| 50 $H_3PO_4$ | 60 | 146 | 126 | 52.2 | 3.39 | 2.39 | 1.54 | 1.55 | 1.30 | 0.89 |
| 5 $H_2C_2O_4$ | 60 | 153 | 113 | 129 | 120 | 49.6 | 30.1 | 3.80 | 1.19 | 0.59 |

[1/] -- as $NH_4VO_3$.

Fig. 1 X 10

Cross Section of Titanium Spot Weld Showing Stress Corrosion Cracking Around Periphery of Weld Nugget After Exposure to Red Fuming Nitric Acid at Room Temperature for Thirty Days.

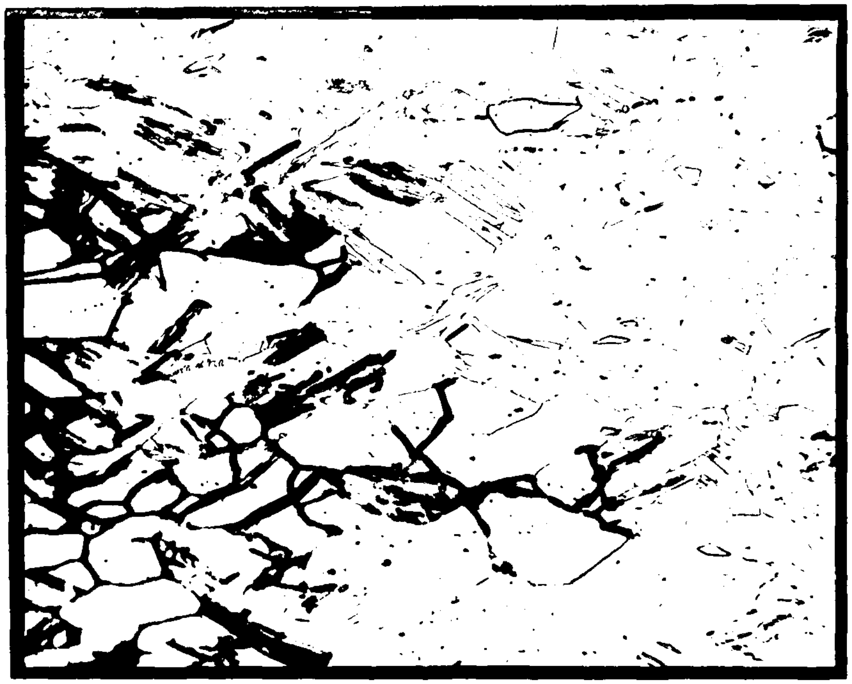

Fig. 2 X 250

Intergranular Corrosion of Titanium Around Periphery of Spot Weld After Exposure to Red Fuming Nitric Acid at Room Temperature for Thirty Days.

U. S. Bureau of Mines
Galvanic Corrosion Laboratory
College Park, Maryland

# Galvanic Corrosion Studies on Titanium and Zirconium Metals

## Quarterly Report for October - December 1953

U. S. Bureau of Mines
Galvanic Corrosion Laboratory
College Park, Maryland

# Galvanic Corrosion Studies on Titanium and Zirconium Metals

D. Schlain, C. Kenahan, and D. V. Steele

Quarterly Report for October - December 1953

## Procedure

The investigation of the galvanic corrosion properties of titanium and zirconium was continued during the past quarter with couple experiments in sulfuric acid, sodium hydroxide, tap water, and synthetic ocean water. All experimental work was done at 35°C. The immersed portion of each metal specimen was 1/4 inch wide and 3 or 3 1/2 inches long. Metal specimens were surfaced with 3/0 emery paper and pumice prior to immersion. In addition to the couple, the test vessels contained uncoupled specimens of each metal. Data obtained included corrosion rates for coupled and uncoupled specimens based upon weight losses as well as galvanic corrosion rates calculated from galvanic currents. Electrode potentials of the couples and of the uncoupled metals were measured with a saturated calomel cell. Non-aerated solution tests were carried out in loosely covered beakers containing 750 milliliters of solution. Helium-aerated or air-aerated solution tests were carried out in sealed vessels with about 500 ml. of solution. The stoppers used in sealing the bottles had openings for gas inlet and outlet, potassium chloride bridge, and four metal specimens. Helium or air was passed through the solution for about one hour prior to immersion of the specimens and continuously during the experiment. The gas was saturated with water vapor at 35°C before entering the specimen bottle, and a water trap was placed after the specimen bottle.

## Results

Titanium is less noble than stainless steels Type 316, and a 20 chromium - 29 nickel type in both helium-aerated and air-aerated 1 and 2 N sulfuric acid solutions (Table 1). Uncoupled specimens of titanium corroded in helium aerated 1 N sulfuric acid but not in the presence of air. Titanium corroded quite rapidly in helium-aerated 2 N sulfuric acid and even more rapidly in air-aerated solution. In every instance, electrical contact with one of the stainless steels greatly decreased the rate at which titanium corroded. Galvanic currents generated in these couples were usually negligible in size. In only one experiment was there a current of appreciable size throughout the 15-day period. This was also the only experiment (with type 316 stainless steel in 2 N $H_2SO_4$, He) in which the total corrosion rate of a coupled titanium specimen was greater than 1 mpy. Type 316 stainless steel corroded slowly in helium-aerated solutions but was quite inert in the presence of air. The 20 chromium -29 nickel stainless steel was inert in both helium-and air-aerated acid solutions. Neither type of stainless steel was affected by electrical contact with titanium in these solutions.

The electrode potentials of zirconium are usually quite similar to those of stainless steels, Type 316 and 20 chromium - 29 nickel, in either helium-aerated or air-aerated 2 N sulfuric acid solution (Table 2).

None of the zirconium-stainless steel couples produced galvanic currents of appreciable size. High purity zirconium was always inert in these environments. However, the lower grade zirconium, coupled or uncoupled, lost weight slowly in helium-aerated solutions. These specimens became dull and blistered in appearance. In air-aerated solutions this type of zirconium was inert when coupled and corroded very slightly when uncoupled. Type 316 stainless steel corroded in helium-aerated 2 N sulfuric acid and in one experiment contact with zirconium appeared to cause a decrease in the corrosion rate. This type of stainless steel, coupled or uncoupled, was quite inert in air-aerated solution. The 20 chromium - 29 nickel stainless steel was generally quite inert in both helium-aerated and air-aerated 2 N sulfuric acid solutions and contact with zirconium had no marked affect.

Zirconium is electropositive (noble) with respect to magnesium in non-aerated 0.008 percent sodium hydroxide solution, College Park, Maryland tap water, and synthetic ocean water (Table 3). Zirconium, uncoupled or in electrical contact with magnesium, was unaffected by these solutions. Magnesium was subject to moderate chemical and galvanic corrosion in sodium hydroxide solution and in tap water. Coupled specimens immersed in tap water were pitted. Uncoupled specimens of magnesium corroded rapidly in synthetic ocean water and contact with zirconium greatly increased the corrosion rate. Both coupled and uncoupled specimens of magnesium were severely pitted. Available data indicate that the corrosion behavior of magnesium is approximately the same in couples with zirconium and titanium.

## Conclusions

1. Little or no galvanic corrosion occurs as a result of contact between titanium or zirconium and one of the stainless steels in 1 or 2 N sulfuric acid solutions.

2. The corrosion rate of titanium decreases as a result of electrical contact with stainless steel in 1 or 2 N sulfuric acid solutions.

3. Zirconium is relatively resistant to 2 N sulfuric acid solutions and is not affected by contact with stainless steel.

4. *Magnesium undergoes very rapid galvanic attack in synthetic* ocean water as a result of contact with zirconium. Galvanic effects are much smaller in tap water and in 0.009 percent sodium hydroxide.

Table 1. Titanium[a]- Stainless Steel Couple Experiments in Sulfuric Acid, 35°C, 15 days

| Normality | Metal | Corrosion Rate, mpy (based on weight loss) |  | Average Galvanic Current, ma | Galvanic Corrosion, mpy (calc. from current) | Electrode potential, volts (referred to standard hydrogen electrode) |  |  |  |
|---|---|---|---|---|---|---|---|---|---|
|  |  | Coupled | Uncoupled |  |  | Coupled |  | Uncoupled |  |
|  |  |  |  |  |  | Initial | Final | Initial | Final |
|  |  |  |  | Flow of Helium |  |  |  |  |  |
| 1 | Ti | 0.6 | 19.5 | 0.04[b] | 1.6 | -0.12 | -0.07 | 0.06 | -0.43 |
|  | S.S., type 316 | 2.7 | 2.2 |  |  | -0.11 | -0.07 | -0.13 | -0.06 |
| 2 | Ti | 4.2 | 26.1 | 0.085 | 2.9 | -0.10 | -0.05 | -0.02 | -0.42 |
|  | S.S., type 316 | 3.4 | 3.5 |  |  | -0.10 | -0.05 | -0.12 | -0.04 |
| 1 | Ti | 0.4 | 16.9 | <0.02 |  | 0.01 | -0.04 | 0.11 | -0.43 |
|  | S.S., 20 Cr 29 Ni | 0.2 | 0.2 |  |  | 0.01 | -0.04 | 0.01 | -0.05 |
| 2 | Ti | 0.8 | 35.3 |  |  | 0.02 | 0.13 | -0.04 | -0.33 |
|  | S.S., 20 Cr 29 Ni | 0.5 | 0.7 | <0.02 |  | 0.02 | 0.13 | 0.02 | 0.20 |
|  |  |  |  | Flow of Air |  |  |  |  |  |
| 1 | Ti | 0.1 | 0.1 | 0.00 | 0.0 | -0.08 | 0.19 | 0.06 | 0.15 |
|  | S.S., type 316 | 0.1 | 0.1 |  |  | -0.08 | 0.19 | -0.11 | 0.49 |
| 2 | Ti | 0.00 | 55.0 | 0.027[c] | 1.0 | -0.09 | 0.50 | 0.10 | -0.28 |
|  | S.S., type 316 | 0.3 | 0.3 |  |  | -0.08 | 0.50 | -0.11 | 0.55 |
| 1 | Ti | 0.1 | 0.6 | <0.02 |  | 0.08 | 0.31 | 0.10 | 0.18 |
|  | S.S., 20 Cr 29 Ni | 0.04 | 0.00 |  |  | 0.08 | 0.31 | 0.14 | 0.05 |
| 2 | Ti | 0.02 | 55.5 | 0.02 | 0.8 | 0.17 | 0.30 | 0.11 | -0.27 |
|  | S.S.,20 Cr 29 Ni | 0.02 | 0.03 |  |  | 0.17 | 0.31 | 0.11 | 0.29 |

Table 1. (continued)

a. Titanium consolidated by arc-melting

b. During initial 7 days of test; galvanic current less than 0.02 ma during remainder of test.

c. During initial 2 days of test; galvanic current less than 0.02 ma during remainder of test.

Table 2. Zirconium-Stainless Steel Couple Experiments in 2N $H_2SO_4$, 35°C, 15 days

| Metal | Corrosion Rate, mpy (based on weight loss) | | Average Galvanic Current, ma | Galvanic Corrosion, mpy (calc. from current) | Electrode Potential, volts (referred to standard hydrogen electrode) | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | Coupled | | Uncoupled | |
| | Coupled | Uncoupled | | | Initial | Final | Initial | Final |
| | | | | Flow of Helium | | | | |
| Zr[a] | 0.04 | 0.00 | | | -0.09 | -0.01 | -0.06 | 0.07 |
| S.S., type 316 | 5.0 | | < 0.02 | | -0.09 | -0.01 | -0.12 | -0.01 |
| Zr[b] | 0.6 | 0.6 | | | -0.09 | -0.02 | -0.19 | -0.08 |
| S.S., type 316 | 5.8 | 11.1 | < 0.02 | | -0.09 | -0.02 | -0.12 | -0.00 |
| Zr[a] | 0.0 | 0.0 | | | 0.02 | 0.04 | -0.07 | -0.41 |
| S.S., 20 Cr 29 Ni | 1.5 | 0.6 | < 0.02 | | 0.02 | 0.04 | 0.00 | 0.03 |
| Zr[b] | 0.5 | 0.5 | | | 0.02 | -0.02 | -0.10 | -0.06 |
| S.S., 20 Cr 29 Ni | 0.1 | 0.2 | < 0.02 | | 0.02 | -0.02 | 0.02 | -0.01 |
| | | | | Flow of Air | | | | |
| Zr[a] | 0.04 | 0.0 | | | -0.09 | 0.59 | -0.09 | 0.41 |
| S.S., type 316 | 0.5 | 0.3 | < 0.02 | | -0.09 | 0.59 | -0.10 | 0.60 |
| Zr[b] | 0.1 | 0.4 | | | -0.09 | 0.35 | -0.09 | 0.09 |
| S.S., type 316 | 0.3 | 0.8 | < 0.02 | | -0.08 | 0.35 | -0.12 | 0.11 |
| Zr[a] | 0.07 | 0.0 | | | 0.17 | 0.33 | -0.06 | 0.11 |
| S.S., 20 Cr 29 Ni | 0.05 | 0.03 | < 0.02 | | 0.17 | 0.33 | 0.10 | 0.22 |
| Zr[b] | 0.07 | 0.2 | | | 0.17 | 0.48 | -0.15 | 0.25 |
| S.S., 20 Cr 29 Ni | 0.03 | 0.04 | 0.00 | | 0.17 | 0.48 | 0.13 | 0.29 |

a. Zirconium metal contained the following impurities, in percent: C 0.02, Fe 0.05, Hf 0.2

b. Zirconium metal contained the following impurities, in percent: C 0.38, Fe 0.74, Hf 1.9 etc.

Table 3. Zirconium[a] - Magnesium Couple Experiments[b], Non-aerated solution, 35°C, 15 days

| Solution | Metal | Corrosion Rate, mpy (based on weight loss) |  | Average Galvanic Current, ma | Galvanic Corrosion, mpy (calc. from current) | Electrode Potential, volts (referred to standard hydrogen electrode) |  |  |  |
|---|---|---|---|---|---|---|---|---|---|
|  |  | Coupled | Uncoupled |  |  | Coupled |  | Uncoupled |  |
|  |  |  |  |  |  | Initial | Final | Initial | Final |
| 0.008 % NaOH | Zr | 0.0 | 0.0 |  |  | -0.95 | -0.30 | -0.46 | 0.10 |
|  | Mg | 10.6 | 5.0 | 0.12 | 7.3 | -0.95 | -0.30 | -1.12 | -0.62 |
| Tap Water[c] | Zr | 0.0 | 0.0 |  |  | -0.95 | -1.00 | -0.41 | 0.09 |
|  | Mg | 27.2 | 4.9 | 0.29 | 18.4 | -0.95 | -1.00 | -1.09 | -0.98 |
| Synthetic Ocean Water[d] | Zr | 0.0 | 0.0 |  |  | -1.31 | -1.32 | -0.35 | -1.09 |
|  | Mg | 2808. | 167. | 27.5 | 1740. | -1.34 | -1.34 | -1.35 | -1.35 |

a. Zirconium metal contained the following impurities, in percent: C 0.02, Fe 0.05, Hf 0.2

b. Carried out in duplicate.

c. Coupled magnesium specimens were pitted.

d. Length of experiment 2 days