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

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Galvanic Corrosion Studies on Titanium and Zirconium Metals

Quarterly Report for April - June 1954

Information not to be disseminated until released by the Director of the Bureau of Mines.

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 April - June 1954

Procedure:

The investigation was continued during the past quarter with titanium-aluminum couple experiments in organic acids. All experimental work was done at 35°C. The immersed portion of each metal specimen was 1/4 inch wide and 3 inches long. Metal specimens were surfaced with 3/0emery 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. Tests with natural aeration 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 more noble than commercially pure aluminum (2 S-0)

in helium-aerated and air-aerated 10 percent formic, acetic, and lactic acids (Tables 1 and 3). Aluminum was consumed at moderate rates by both chemical and galvanic action in these environments. Corrosion rates were higher in the presence of air. Titanium was inert in acetic and lactic acid solutions and this resistance was not affected by contact with aluminum or by the type of aeration. Uncoupled specimens of titanium did not show weight losses in formic acid solutions but electrical contact with aluminum in helium-aerated solutions caused the metal to corrode slowly. Only a small weight loss occurred in this acid with natural aeration (Table 2) and there was no weight loss with a flow of air.

Titanium is initially the cathodic member of the titaniumaluminum couple in both 1 and 9 percent ckalic acid solutions with any of the three types of aeration, but generally becomes anodic after a period of immersion. In helium-aerated solutions this reversal in the direction of flow of the galvanic current is generally accompanied by a shift in the relative positions of the time-potential curves. However, in airaerated solutions single (uncoupled) specimens of titanium always retain more noble electrode potentials than aluminum in spite of the change in the direction of current flow. Even in solutions with natural aeration single titanium specimens sometimes remain slightly more positive than aluminum throughout the test period.

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Galvanic corrosion rates were moderate for both titanium and aluminum and were generally higher in the more concentrated solutions. Chemical corrosion rates for aluminum increased with acid concentration and the presence of air. These rates were not greatly affected by placing the aluminum in contact with titanium. Uncoupled specimens of titanium corroded in helium-aerated solutions of oxalic acids and in solutions with

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natural aeration. Titanium was resistant to air-aerated 1 and 9 percent exalic acid solutions when uncoupled but underwent moderate chemical corrosion as a result of contact with aluminum. Titanium consolidated by powder metallurgy techniques has about the same corrosion properties as the arc-melted metal in exalic acid solutions. However, corrosion rates are generally higher for titanium prepared from powder.

Titanium is more noble than aluminum in helium-aerated and airaerated 1% tartaric and 10% citric acid solutions. However, galvanic currents were always small or negligible in size. Titanium was inert in this environment and aluminum corroded very slightly. The weight losses of these metals were not affected by contact.

Conclusions:

1. Uncoupled specimens of titanium are resistant to air-aerated solutions of 1 and 9 percent oxalic acid solutions but contact with aluminum in these environments causes both chemical and galvanic corrosion of titanium. In the absence of air or with limited supply of air, both titanium and aluminum are consumed by chemical and galvanic action in these solutions.

2. Titanium, ordinarily resistant to chemical corrosion in 10 percent formic acid even in the absence of air, undergoes some chemical attack as a result of contact with aluminum.

3. Titanium is resistant to chemical and galvanic corrosion in 10 percent acetic, lactic, and citric acids and to 1 percent tartaric acid.

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Table 1. Titanium-Aluminum^a Couple Experiments in Organic Acids, 35°C, 15 days

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Solution	Metal	Corrosion Rate, (based on weight loss) Coupled Uncoupl	Corrosion Rate, mpy (based on weight loss) Coupled Uncoupled	Average Galvanic Current, ma	Galvanic Corrosion, mpy (calc. from current)	Ele (referred Coup Initial	Electrode Pot red to standar Coupled 1 Final	Electrode Potential, volts (referred to standard hydrogen electrode) Coupled Uncoupled Initial Final Initial Final	volts gen electrode) Uncoupled al Final
				Flow	Flow of helium				
10 percent Formic Acid	11	0 . 8	0.0	11.0	2•5	-0.48 -0.49	۲۹•0- ۲۹•0-	0 .02 -0.23	다.
10 percent Formic Acid	11	1.3 9.5	0°0 9•4	0•095	2.1	-0-119 -0.50	-0-11L -011L	-0.11 -0.20	-0.22 -0.15
10 percent Acetic Acid	14	0 ° 0 2 ° 1	0°0 1°2	0.04	1.5	-0.34 -0.34	-0-141-0-	-0.08 -0.28	0,10 -0,51
10 percent Lactic Acid	11	0 . 0 2 . 8	0 .1 2 . 8	0•03	1.2	-0.30	-0-40 -0.40	-0.15 -0.26	-0°09 -0,14
l percent Oxalic Acid ^b	11	9 .3 13.4	13.1	0 . 04 0 . 18	1.7 6.1	-0.52 -0.52	-0.46 -0.46	0.09	-0-lt7 -0-lt7
l percent Oxalic Acid ^{c,d}	11	55 .8 25 .6	45 5 25 •4	0.40 0.24	15•4 8•7	-0.19 -0.50	61.0- 51.0-	-0.08 -0.39	11-0-
l percent Oxalic Acid ^{c,d}	11	51.7 25.4	51.7 25.5	0.56 0.27	21.8 9.9	-0-149 -0.149	-0°†0 -0°†0	-0.02 -0.23	-()12 -0 - 38
9 percent Oxalic Acid ^b	1 4	19.7 21.2	22•4 19•5	0.096 0.172	2•9 4•2	-0°47	17°0-	0.04 -0.27	-0.39
9 percent Oxalic Acid ^c	1 .4	75.0 22.7	68.7 21.5	0•23	6 . 8	-0-15 -0.15	-0°†0 -0°†0	0.01 -0.24	-0-40 -0-42
l percent Tartaric Acid ^e	11	0 . 0 2 . 1	0.0 1.7	0.02 0.03	0.8 1.1	-0.28 -0.29	-0°†0	-0.18 -0.26	-0°12 -0,114
10 percent Citric Acid	11	0°0 1•1	0°0 1°0			-0.22 -0.22	-0.35 -0.35	-0.06 -0.22	-0-09 1-1-0-

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Table 1. (continued)

^a Titanium consolidated by arc-melting except as noted; aluminum 2 S-O

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- Aluminum was anodic during first 9 or 10 days of immersion, titanium was ano ic during remainder of experiment. م
- c Titanium consolidated by powder metallurgy techniques.
- Aluminum was anodic during first 2.3 days of immersion, titanium was anodic during remainder of experiment. ъ
- Aluminum was anodic during first 2 days and titanium was anodic during 5 days. ø

Table 2. Titanium-Aluminum^a Couple Experiments in Organic Acids, 35°C, 15 days

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Solution	Metal	Corrosion (based on	Rate, mpy weight loss)	Average Galvanic Current,	Galvanic Corrosion, mpy (calc.	Elec (referred t	ctrode Pote o standard bled	Electrode Potential, volts (referred to standard hydrogen electrode) Coupled	s Lectrode) Ipled
		pardnon	uncoupled	gu	from current)	Initial	Final	Initial	Final
				Natural	Natural aeration				
10 percent Formic Acid	11	0 . 3 13.6	0.0 13.0	0.18	6 . 6	-0.37 -0.37	0 ، ا د ا	-0°06 -0°10	0-01 10-0
l percent Oxalic ≠cid ^b	24	16 .1 38 .1	18.7 37.7	0.14	5•7 9•0	-0.52 -0.52	-0.10 -0.04	-0.05 -0.57	-0.05 -0.09
<i>9</i> percent Oxalic Acid ^c	ដ 4	34.3 36.9	4.3.7 4.3.4	75.0	13.7	-0.17 -0.118	-0-01 -0.03	-0,01 -0,51	-0.15 -0.03
l percent Oxalic Acid ^{b,d}	됩	27 . 9 42 .1	32°9 14.5	0°03 0°11	1.2 4.0	-0.48 -0.48	60°0-	15°0-	-0 . 10
9 percent Oxalic Acidesd	ĩa	81.8 36.8	0.0 141.9	0_8 0_5	32 . 3 17 . 2	-0.43 -0.42	0-0- 20.0- 20.0	-0.01 -0.50	0.02 -0.03
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^a Titanium consolidated by arc-melting except as noted; aluminum 2 S-O

Aluminum was anodic during first 2 to 7 days, titanium was anodic during remainder of experiment. م

Aluminum was anodic during 10 to 20 hours, titanium was anodic during remainder of experiment. υ

d Titanium consolidated by powder metallurgy techniques.

Titanium-Aluminum^a Couple Experiments in Organic Acids, 35°C, 15 days Table 3.

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(referred to standard hydrogen electrode) 0.39 0.19 Final 0.58 0.58 0.09 0.13 0.00 0.35 0.18 -0.13 0 र र न र 200 0.35 0.06 ч. С. С. Uncoupled Electrode Potential, volts Initial 0.02 00 88 89 -0.02 0.02 0.0 -0-8 28 0.00 0.25.0 -0.19 -0.05 9 0 9 E -0.26 0.0 -0.18 -0.10 60°0 00 88 -0.16 10.0--0.16 -0.15 -0.15 Final -0.17 -0.17 -0.07 -0.07 -0-11 -0.11 -0.01 -0.11 -0.01 Coupled Initial -0.36 -0.36 0.31 -0.20 -0-13 0-1-0--0-38 -0-10 -0-38 -0-38 11-0-0--0.23 -0.23 -0.23 -0-11-0-ສ•0mpy (calc. from current) Corrosion, Galvanic 6.0 4.0 7.4 3**.**1 8.2 1.5 1.6 7.6 1.1 1.7 Flow of air Galvanic Current, Average BUR 0.12 0.20 0.10 0.17 0,04 11.0 **ರ**ನ 0 0.28 0.08 0.08 0. S **ದ**ಂ Corrosion Rate, mpy Uncoupled 0.09 56.2 1038) (based on weight 0.0 0.0 0°0 0°0 0 0 3.9 0.0 10.5 10.5 0.0 2.6 0.0 1.14 0.lt 58.7 0**.**4 52**.**6 1.4 Coupled 0.0 0.0 0°0 0.61 7.84 10.8 8**.1** 53**.**8 15.6 13.8 57.2 20.02 0°0 2.8 0.0 1.5 Metal 14 24 24 ゴロ はね れれ ねれ H 11 27 **1**4 4 Al Oxalic Acide,d Tartaric Acid Oxalic Acid^b Oxalic Acid^c Oxalic Acid^e Formic Acid Acetic Acid Lactic Acid Oxalic Acid Oxalic Acid **Citric** Acid Solution 10 percent 10 percent 10 percent 10 percent 9 percent 9 percent 1 percent 1 percent 1 percent 9 percent 1 percent

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Table 3. (continued)

- ^a Titanium consolidated by arc-melting except as noted; aluminum 2 S-0
- Aluminum was anodic during itrst 5 days of experiment, titanium was anodic during remainder of test. م
- c Titanium consolidated by powder metallurgy techniques
- Aluminum was anodic during first 25 days of experiment; titanium was anodic during 11 days. Ъ
- Aluminum was anodic during first 6 days of experiment, titanium was anodic during remainder of experiment. ø