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CORROSION STUDIES ON

TITANIUM AND ZIRCONIUM METALS

Semiannual Report December 1949

401/10-22

SEMI-ANNUAL REPORT

December, 1949

Corrosion Studies on Titanium and Zirconium Metals

L. B. Golden, I. R. Lane, and W. Mace

This investigation was initiated in June, 1947, to obtain quantitative data on the corrosion resistance of titanium and zirconium metals and their alloys to acids, bases, and salts. Since, from the utilitarian viewpoint, titanium may become a successful replacement for stainless steel, two of the more corrosion-resistant varieties, type 316 and Carpenter No. 20, have been used in parallel tests to obtain a basis for comparison. Also, since, for certain purposes, zirconium may become a replacement for the much less abundant tantalum metal, extensive tests have been made on the corrosion resistance of this metal.

During the past six months tests have been made on the corrosion resistance of titanium in solutions of phosphoric, hydrochloric, sulfuric, and nitric acids; also in mixtures of concentrated sulfuric and nitric acids. Titanium, zirconium, and stainless steels were tested in water-saturated chlorine gas and in chlorine-saturated water. The following compounds were used in carrying out tests on titanium and zirconium: ferric, cupric, mercuric, calcium, aluminum, zinc, and magnesium chlorides, and oxalic, formic, lactic, tartaric and tannic acids. A discussion of the various tests follows.

Titanium - phosphoric acid:

Titanium was tested in various concentrations of aerated phosphoric acid for six days at three different temperatures, 35°, 60°, and 100° C.

Corrosion rates at 35° C ranged from a low of 0.13 mils per year in a 5 percent solution of the acid to a high of 29.7 mils per year in the concentrated (85 percent) acid. (See Table I). At 60° C rates varied from 0.74 m.p.y. in 5 percent acid to 367 m.p.y. in 85 percent acid. The corrosion resistance of titanium to phosphoric acid solutions at 100° C was very poor, since even in the 5 percent acid solution the rate was 202 m.p.y. When the concentration of the acid was raised to 50 percent, the rate was 1845 m.p.y.

Titanium - hydrochloric acid:

Titanium was tested in various concentrations of aerated hydrochloric acid for six days at 35°, 60°, and 100° C. At 35° C corrosion rates were not appreciable until the concentration of acid exceeded 6 percent (Table I). Rates at 60° C ranged from 0.11 m.p.y. in 1 percent acid to 1098 m.p.y. in 20 percent acid. At 100° C rates varied from 0.35 m.p.y. in 0.5 percent acid to 938 m.p.y. in 4 percent acid.

Titanium - sulfuric acid:

Titanium was tested at 35° C in various concentrations of sulfuric acid which were kept saturated with oxygen-free nitrogen. Rates ranged from 8.00 m.p.y. in 5 percent acid to a maximum of 1640 m.p.y. in 80 percent acid (Table II).

Titanium - nitric acid:

Titanium was tested at 60° C in various concentrations of aerated nitric acid. Corrosion rates were all less than 1 m.p.y. (Table II).

Titanium - sulfuric and nitric acid mixtures:

Titanium samples were tested in non-aerated and static mixtures of concentrated (96.5 percent) sulfuric acid and concentrated (69.5 percent) nitric acid at 35°, 60°, and 100° C. At 35° C corrosion rates ranged from a maximum of 10.6 mils per year in a mixture of 99 percent sulfuric - 1 percent nitric acid to a minimum of 0.28 mils per year in 1 percent sulfuric - 99 percent nitric acid. When the concentration of sulfuric acid dropped below 50 percent the corrosion rates were all less than 1 mil per year (Table III). Colored oxide films were observed on all samples tested within the range of 80 percent sulfuric - 20 percent nitric acid to 20 percent sulfuric - 80 percent nitric acid.

Corrosion rates at 60° C ranged from a minimum of 0.10 mils per year in a mixture of 1 percent sulfuric - 99 percent nitric acid to a maximum of 75.0 mils per year in 99 percent sulfuric - 1 percent nitric acid. At 100° C rates ranged from 0.65 to 1000 m.p.y. over the same range of acid concentrations as those used at 60° C. When the concentration of sulfuric acid fell below 70 percent in the mixture of the two acids at 60° C, titanium was satisfactorily resistant. However, at 100° C the concentration of sulfuric acid above which the metal corroded excessively was only 30 percent. Colored oxide films were observed on all samples tested at 60° C and 100° C within the range of 80 percent sulfuric - 20 percent nitric acid to 1 percent sulfuric - 99 percent nitric acid.

Titanium - inorganic chlorides:

Titanium was tested in aerated solutions of magnesium, ferric, cupric, and mercuric chlorides in concentrations ranging from 1 to 20 percent and at three different temperatures, 35°, 60°, and 100° C. Corrosion rates in all instances were negligible (Table IV). Tests in aerated 5 and 10 percent calcium chloride at 35° C gave negligible rates, but when the metal was tested in 10 percent calcium chloride at 100° C one of the four samples tested had two large, deep pits which penetrated about halfway through the sample and which were filled with a white substance (presumably titanium dioxide). Other much smaller pits were also present. The corrosion rate for this sample was 3.74 mils per year. The same type of pitting was observed when titanium was tested in 25 percent calcium chloride solution at 100° C. Although the average corrosion rate was very low (0.61 m.p.y.), there were present about six fairly large pits per sample, some being quite deep, penetrating about halfway through the samples (i.e. about 0.020 inches deep).

Tests in aerated 5 and 10 percent aluminum chloride solutions at 35° C and in 10 percent aluminum chloride at 100° C gave zero or negligible corrosion rates. However, in 25 percent aluminum chloride at 100° C, titanium was severely corroded. Three out of four samples were evenly corroded while the fourth contained numerous shallow pits similar to those formed in calcium chloride solutions.

Tests in aerated 5 and 20 percent zinc chloride solutions at 35°, 60°, and 100° C gave negligible corrosion rates. Although the corrosion rate for titanium in boiling 5 percent zinc chloride solution was zero since no weight loss occurred, numerous small pits were present on the surfaces of the samples. However, pitting was not as severe as that which had occurred in 25 percent calcium chloride solution at 100° C.

Titanium, zirconium, and stainless steels - chlorine- saturated water and water-saturated chlorine:

Titanium, zirconium, and type 316 and Carpenter 20 stainless steels were tested at room temperature totally immersed in chlorine-saturated water for a period of 172 hours. Corrosion rates for titanium and zirconium were negligible, those for Carpenter 20 stainless steel very low, while the rates for type 316 stainless steel were appreciable (Table V).

However, when these metals and alloys were tested in an atmosphere of water-saturated chlorine, marked differences in corrosion resistance were observed. Titanium showed no evidence of corrosion with the exception of a very slight loss in weight. On the other hand, zirconium was only slightly resistant to an attack which was characterized by the formation on the surface of the metal of a voluminous moss-like or fungous-like grey-colored corrosion product. The underlying metal was badly pitted and in several instances the pits penetrated entirely through the sample. Zirconium metal prepared by the Foote Mineral Company (iodide process) was subjected to the same test and results similar to those with Bureau of Mines (magnesium reduction process) zirconium were obtained (Figures I-IV).

Titanium, zirconium, and stainless steel - oxalic acid:

Titanium exhibited poor corrosion resistance to even very dilute solutions of aerated oxalic acid at elevated temperatures (Table VI). Even a 0.5 percent acid solution at 60° C gave a rate of 94.5 mils per year and higher percentages and temperatures gave correspondingly greater corrosion rates. In contrast, zirconium gave very low rates (less than 0.50 m.p.y.) in all concentrations of acid tested. In the concentrations tested, Carpenter 20 stainless steel resisted the corrosive action of oxalic acid much better than titanium.

Titanium, zirconium, and stainless steel - formic acid:

Titanium showed negligible corrosion rates when tested in aerated 90 percent formic acid at 60° C, and in aerated 25 and 50 percent formic acid at 100° C (Table VI). However, when tested in boiling (non-aerated)

25, 50, and 90 percent formic acid, corrosion rates were 96.0, 300, and 118 mils per years, respectively. These tests clearly demonstrate the important part played by oxygen in inhibiting corrosion under certain conditions. Zirconium gave rates of less than 0.2 m.p.y. for all concentrations of acid tested and Carpenter 20 stainless steel less than 7.0 m.p.y.

Titanium, zirconium, and stainless steel - lactic acid:

Titanium, zirconium, and Carpenter 20 stainless steel were each tested in various concentrations of aerated lactic acid. The only appreciable corrosion rate (12.2 m.p.y.) was that shown by the stainless steel in boiling 85 percent acid (Table VI).

Titanium, zirconium, and stainless steel - tartaric acid:

Titanium, zirconium, and Carpenter 20 stainless steel were each tested in various concentrations of aerated tartaric acid at 35° C. Corrosion rates were zero or negligible (Table VI).

Titanium and stainless steel - tannic acid:

Titanium and Carpenter 20 stainless steel showed zero or negligible corrosion rates when tested in 25 percent tannic acid solution (Table VI).

Zirconium and stainless steel - inorganic chlorides:

Zirconium and Carpenter 20 stainless steel were both tested in aerated solutions of calcium, aluminum, zinc, and magnesium chlorides in concentrations ranging from 5 to 20 percent and at three different temperatures, 35°, 60°, and 100° C. At 35° C rates for both metals were negligible. (See Table VII). Rates for zirconium were zero or negligible in all solutions tested at 60° and 100° C. Carpenter No. 20 stainless steel was appreciably corroded by 10 percent aluminum chloride solution at 60° and 100° C and by 5 percent zinc chloride solution at 100° C.

Titanium and zirconium - sulfurous acid:

Titanium and zirconium samples were tested in sulfurous acid (6 percent solution of sulfur dioxide) at 60° C and 100° C. The tests were carried out under pressure in sealed glass tubes to prevent the loss of any sulfur dioxide from solution at these temperatures. Corrosion rates were negligible.

Titanium, zirconium, and stainless steel - boiling chromic acid:

Titanium, zirconium, and Carpenter 20 stainless steel were each tested in boiling chromic acid (10 percent CrO_3) for a period of eleven days. The corrosion rates for the three metals were, respectively, 0.04, 0.00, and 91.0 mils per year.

Zirconium - nitric acid:

Tests were made on zirconium in 10, 20, 30, 40, and 50 percent nitric acid solutions at 60° C. Rates were all negligible (0.00 - 0.10 m.p.y.)

Zirconium - boiling nitric acid test (Huey test):

Zirconium was tested in boiling 65 percent nitric acid for one 24-hour and four 48-hour test periods. Corrosion rates for the successive periods were 0.44, 0.04, 0.08, 0.00, and 0.00 m.p.y., respectively, giving an average of 0.11 m.p.y.

Zirconium - phosphoric acid:

Zirconium was tested in boiling 85 percent phosphoric acid for six days. The corrosion rate was very high (739 m.p.y.).

Stainless steel - boiling red fuming nitric acid:

Carpenter No. 20 stainless steel, when tested in boiling red fuming nitric acid for a period of eleven days, showed a corrosion rate of 16.1 mils per year. Identical tests using titanium and zirconium metals gave rates of

0.26 and 0.29 mils per year, respectively.

* * *

Future program:

The program for the immediate future will include a continuation of tests on titanium and zirconium metals with inorganic and organic acids and solutions of salts and bases at different concentrations and temperatures. Tests have just been started on the corrosion resistance of a series of titanium-zirconium alloys to materials used for rocket fuels. Simulated marine atmosphere tests (salt spray) will also be made. Galvanic corrosion research will be conducted on titanium and zirconium and their alloys.

TABLE I

Titanium - Inorganic Acids (with aeration)

Test Solution (percent by weight)	Average corrosion rate 6-day run, mils per year		
	35° C	60° C	100° C
1.0 H_3PO_4	--	--	0.12
3.0 H_3PO_4	--	--	62.0
5.0 H_3PO_4	0.13	0.74	202
10 H_3PO_4	0.30	1.50	455
15 H_3PO_4	--	--	480
20 H_3PO_4	0.60	13.7	685
30 H_3PO_4	0.77	59.0	1040
32.5 H_3PO_4	5.64	--	--
35 H_3PO_4	5.80	--	--
37.5 H_3PO_4	8.40	--	--
40 H_3PO_4	13.4	128	1550
50 H_3PO_4	18.5	179	1845
60 H_3PO_4	22.4	239	--
70 H_3PO_4	26.8	280	--
80 H_3PO_4	29.0	340	--
85 H_3PO_4	29.7	367	--
0.5 HCl	--	--	0.35
1.0 HCl	0.23	0.11	18.5
1.5 HCl	--	--	173
2.0 HCl	--	0.64	272
2.5 HCl	--	--	444
3.0 HCl	0.29	0.38	696
3.5 HCl	--	--	689
4.0 HCl	--	42.6	938
5.0 HCl	1.46	42.5	--
6.0 HCl	2.44	131	--
7.0 HCl	--	176	--
7.5 HCl	20.8	--	--
10.0 HCl	40.1	351	--
12.5 HCl	59.5	604	--
15.0 HCl	96.7	789	--
17.5 HCl	122	--	--
20.0 HCl	175	1096	--

TABLE II

Titanium - Inorganic Acids

Test solution (percent by weight)	Temperature °C	Aeration	Average corrosion rate, 6-day run, mils per year
5 H_2SO_4	35	N_2 - sat'd.	8.00
10 H_2SO_4	35	N_2 - sat'd.	47.5
20 H_2SO_4	35	N_2 - sat'd.	60.4
30 H_2SO_4	35	N_2 - sat'd.	152
40 H_2SO_4	35	N_2 - sat'd.	264
50 H_2SO_4	35	N_2 - sat'd.	95
60 H_2SO_4	35	N_2 - sat'd.	29.6
65 H_2SO_4	35	N_2 - sat'd.	16.9
70 H_2SO_4	35	N_2 - sat'd.	38.0
75 H_2SO_4	35	N_2 - sat'd.	1620 #
80 H_2SO_4	35	N_2 - sat'd.	1640 *
85 H_2SO_4	35	N_2 - sat'd.	790
90 H_2SO_4	35	N_2 - sat'd.	493
96.5 H_2SO_4	35	N_2 - sat'd.	216
10 HNO_3	60	air - sat'd.	0.48
20 HNO_3	60	air - sat'd.	0.67
30 HNO_3	60	air - sat'd.	0.85
40 HNO_3	60	air - sat'd.	0.69
50 HNO_3	60	air - sat'd.	0.40
60 HNO_3	60	air - sat'd.	0.33
70.4 HNO_3	60	air - sat'd.	0.31

73-hour run
* 48-hour run

TABLE III

Titanium - Sulfuric and Nitric Acid Mixtures

Test Solution* (percent by weight)	Average corrosion rate 6-day run, mils per year		
	35° C	60° C	100° C
100 H_2SO_4 + 0 HNO_3	209	--	--
99 H_2SO_4 + 1 HNO_3	10.6	75.0	1000
95 H_2SO_4 + 5 HNO_3	8.31	74.4	1060
90 H_2SO_4 + 10 HNO_3	8.80	68.9	1050
80 H_2SO_4 + 20 HNO_3	9.50	62.5	927
70 H_2SO_4 + 30 HNO_3	5.68	49.1	759
60 H_2SO_4 + 40 HNO_3	3.76	32.8	585
50 H_2SO_4 + 50 HNO_3	1.42	15.7	265
40 H_2SO_4 + 60 HNO_3	0.66	6.15	106
30 H_2SO_4 + 70 HNO_3	0.34	2.36	37.0
20 H_2SO_4 + 80 HNO_3	0.38	1.83	12.5
10 H_2SO_4 + 90 HNO_3	0.34	0.45	3.89
5 H_2SO_4 + 95 HNO_3	0.28	0.20	1.85
1 H_2SO_4 + 99 HNO_3	0.28	0.10	0.65
0 H_2SO_4 + 100 HNO_3	0.45	0.31	--

* All solutions non-aerated and static

TABLE IV

Titanium - Inorganic Chlorides (with aeration)

Test Solution (percent by weight)	Average corrosion rate 6-day run, mils per year		
	35° C	60° C	100° C
1 $FeCl_3$	0.02	--	0.00
5 $FeCl_3$	0.09	--	0.03
10 $FeCl_3$	0.00	--	0.09
15 $FeCl_3$	0.10	--	0.13
20 $FeCl_3$	0.13	--	0.13
1 $CuCl_2$	0.14	--	--
5 $CuCl_2$	0.18	--	--
10 $CuCl_2$	0.02	--	--
15 $CuCl_2$	0.02	--	--
1 $HgCl_2$	0.02	--	--
5 $HgCl_2$	0.05	0.00	--
10 $HgCl_2$	--	--	0.04
sat'd. sol'n. $HgCl_2$	0.05	0.00	0.04
5 $CaCl_2$	0.00	--	--
10 $CaCl_2$	0.07	--	0.29
25 $CaCl_2$	--	--	0.61
5 $AlCl_3$	0.00	--	--
10 $AlCl_3$	0.00	--	0.09
25 $AlCl_3$	--	--	258
5 $ZnCl_2$	0.06	0.00	0.20 (0.00*)
20 $ZnCl_2$	0.05	0.24	0.10
5 $MgCl_2$	0.00	0.00	--
20 $MgCl_2$	0.14	--	--

* Boiling and non-aerated

TABLE V

Titanium, Zirconium, and Stainless Steels - Chlorine (Room Temperature)

Metal	Test Solution (percent by weight)	Average corrosion rate 172-hr. run, mils per year
C.R. Ti 1/	Cl_2 saturated H_2O	0.10
C.R. Zr 2/	Cl_2 saturated H_2O	0.56
316 S.S. 3/	Cl_2 saturated H_2O	15.4
20 S.S. 4/	Cl_2 saturated H_2O	1.46
C.R. Ti	H_2O saturated Cl_2	0.07
C.R. Zr	H_2O saturated Cl_2	192
316 S.S.	H_2O saturated Cl_2	527
20 S.S.	H_2O saturated Cl_2	478

1/ Cold rolled titanium
2/ Cold rolled zirconium
3/ Type 316 stainless steel
4/ Carpenter 20 stainless steel

TABLE VI

Titanium, Zirconium and Stainless Steel - Organic Acids (with aeration)

Metal	Test Solution (percent by weight)	Average corrosion rate 6-day run, mils per year			
		35° C	60° C	100° C	Boiling#
C.R. Ti 1/	0.5 oxalic	0.55	94.5	82.0	--
C.R. Ti	1 oxalic	5.96	177	828*	--
C.R. Zr 2/	1 oxalic	0.13	0.20	--	--
20 S.S. 3/	1 oxalic	0.08	1.30	--	--
C.R. Ti	5 oxalic	4.94	368	1290*	--
C.R. Zr	5 oxalic	0.29	0.30	--	--
20 S.S.	5 oxalic	0.25	2.67	--	--
C.R. Ti	10 oxalic	0.58	450	1240*	--
C.R. Zr	10 oxalic	0.48	--	--	--
20 S.S.	10 oxalic	0.19	--	--	--
C.R. Ti	25 oxalic	--	470	1945*	--
C.R. Ti	10 formic	--	--	0.18	0.00
C.R. Zr	10 formic	--	--	--	0.00
20 S.S.	10 formic	--	--	--	6.30
C.R. Ti	25 formic	--	--	0.04	96.0
C.R. Zr	25 formic	--	--	--	0.09
20 S.S.	25 formic	--	--	--	6.27
C.R. Ti	50 formic	--	--	0.04	300
C.R. Zr	50 formic	--	--	--	0.19
20 S.S.	50 formic	--	--	--	1.92
C.R. Ti	90 formic	0.03	0.01	--	118
C.R. Zr	90 formic	0.12	--	--	0.16
20 S.S.	90 formic	0.17	--	--	1.11
C.R. Ti	25 lactic	0.03	--	--	--
C.R. Zr	25 lactic	0.03	--	--	--
C.R. Ti	50 lactic	0.08	--	--	--
C.R. Zr	50 lactic	0.00	--	--	--
C.R. Ti	85 lactic	0.00	--	0.33	0.40
C.R. Zr	85 lactic	0.00	--	--	0.09
20 S.S.	85 lactic	0.00	--	--	12.2
C.R. Ti	10 tartaric	0.00	--	--	--
C.R. Zr	10 tartaric	0.00	--	--	--
20 S.S.	10 tartaric	0.00	--	--	--
C.R. Ti	25 tartaric	0.00	--	--	--
C.R. Zr	25 tartaric	0.00	--	--	--
20 S.S.	25 tartaric	0.07	--	--	--
C.R. Ti	50 tartaric	0.08	--	--	--
20 S.S.	50 tartaric	0.08	--	--	--
C.R. Ti	25 tannic	0.00	0.00	0.00	--
20 S.S.	25 tannic	0.00	0.00	0.29	--

1/ Cold rolled titanium
2/ Cold rolled zirconium
3/ Carpenter 20 stainless steel

* three-day run
\# boiling solutions were non-aerated

TABLE VII

Zirconium and Stainless Steel - Inorganic Chlorides (with aeration)

Metal	Test solution (percent by weight)	Average corrosion rate 6-day run, mils per year		
		35° C	60° C	100° C
C.R. Zr[1/]	5 $CaCl_2$	0.00	--	--
C.R. Zr	10 $CaCl_2$	0.00	0.00	0.00
20 S.S.[2/]	10 $CaCl_2$	0.01	0.04	0.11
C.R. Zr	5 $AlCl_3$	0.00	--	--
C.R. Zr	10 $AlCl_3$	0.02	0.00	0.00
20 S.S.	10 $AlCl_3$	0.39	14.4	45.2
C.R. Zr	5 $ZnCl_2$	0.01	0.08	0.04(0.00*)
20 S.S.	5 $ZnCl_2$	0.04	0.15	31.3(6.05*)
C.R. Zr	20 $ZnCl_2$	0.02	--	--
20 S.S.	20 $ZnCl_2$	0.05	--	--
C.R. Zr	5 $MgCl_2$	0.02	0.00	--
20 S.S.	5 $MgCl_2$	0.07	0.00	--
C.R. Zr	20 $MgCl_2$	0.15	0.00	--
20 S.S.	20 $MgCl_2$	0.09	--	--

1/ Cold rolled zirconium
2/ Carpenter 20 stainless steel

* boiling and non-aerated

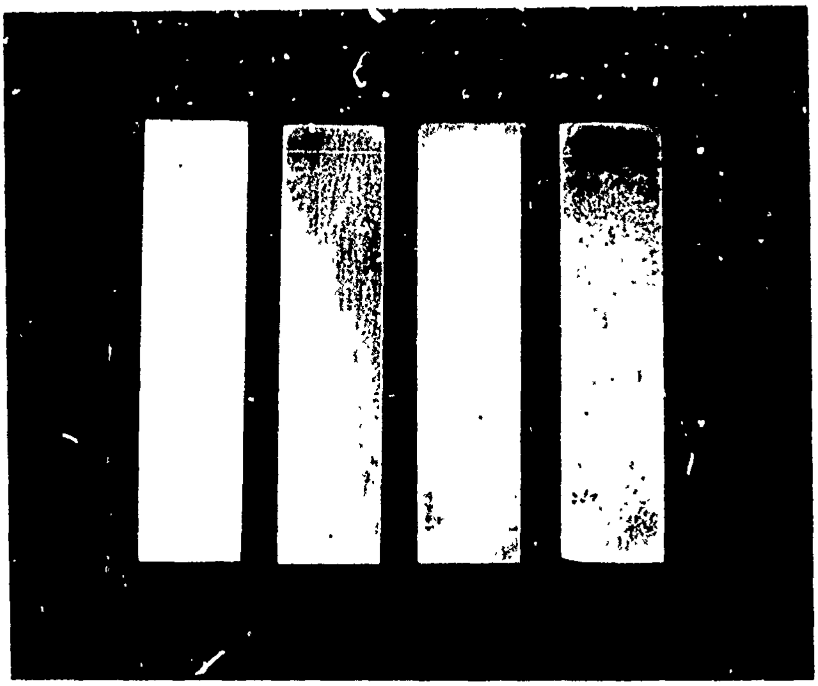

Fig. 1 X1

Titanium after 172 hours exposure in an atmosphere of water-saturated chlorine. Average corrosion rate was 0.07 mils per year.

Fig. 2 X1

Zirconium after 172 hours exposure in an atmosphere of water-saturated chlorine. Average corrosion rate was 192 mils per year.

Fig. 3 X1
Type 316 stainless steel after 172 hours exposure in an atmosphere of water-saturated chlorine. Average corrosion rate was 527 mils per year.

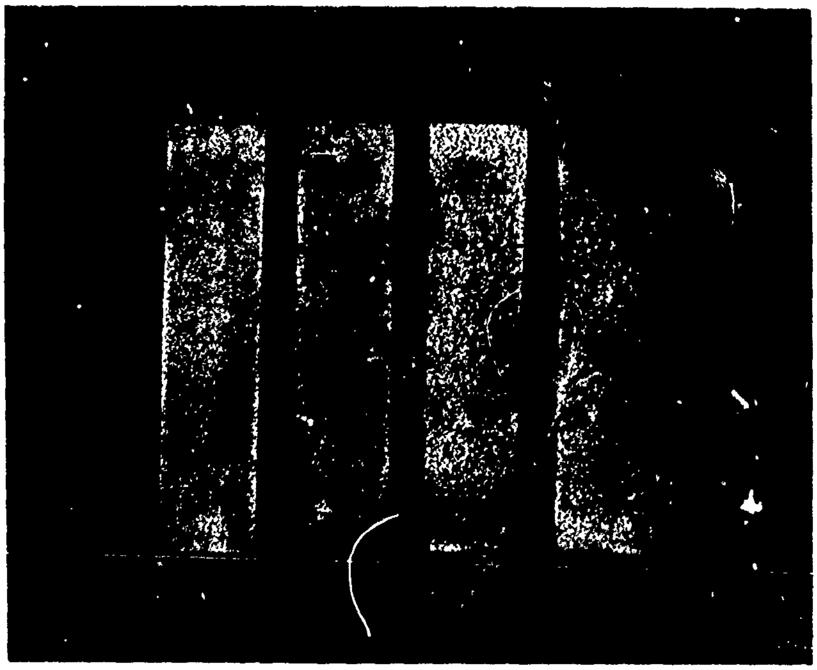

Fig. 4 X1
Carpenter No. 20 stainless steel after 172 hours exposure in an atmosphere of water-saturated chlorine. Average corrosion rate was 473 mils per year.