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THE EFFECT OF URANIUM ADDITIONS ON THE CORROSION BEHAVIOUR OF AISI TYPE 430 STAINLESS STEEL

by

G. J. Biefer*

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ABSTRACT

AISI Type 430 stainless steels, and similar steels with 0.017-3.11% uranium, were subjected to laboratory corrosion tests in several aqueous solutions. The results indicated that uranium additions in the range 0.1-0.5% brought about improvements in corrosion resistance. To determine whether the laboratory results are correlated with improved corrosion resistance under service conditions, AISI Type 430 steels with 0%, 0.25% and 0.5% uranium are undergoing long-term field tests.

*Head, Corrosion Section, Physical Metallurgy Division, Mines Branch, Department of Mines and Technical Surveys, Ottawa, Canada.

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L'EFFET DE L'ADDITION D'URANIUM SUR LE COMPORTEMENT À LA CORROSION DE L'ACIER INOXYDABLE DE TYPE AISI 430

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G. J. Biefer*

RÉSUMÉ

Des aciers inoxydables de type AISI 430 et des aciers semblables alliés à 0.017 à 3.11 p. 100 d'uranium ont été soumis en laboratoire à des essais de corrosion en solutions aqueuses. Les résultats indiquent que des additions d'uranium variant de 0.1 à 0.5 p. 100 améliorent la résistance à la corrosion. Pour déterminer si les résultats obtenus au laboratoire seront confirmés par une résistance accrue à la corrosion dans la pratique, on est à faire subir des épreuves à long terme sur place à des aciers de type AISI 430 contenant 0, 0.25 et 0.5 p. 100 d'uranium.

*Chef, Section de la corrosion, Division de la métallurgie physique, Direction des mines, ministère des Mines et des Relevés techniques, Ottawa, Canada.

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INTRODUCTION

A decreased demand for Canadian uranium, and consequent excess productive capacity, stimulated a combined effort by Canadian government and industry to develop new non-nuclear uses for this element. In the Physical Metallurgy Division, uranium-bearing steels were produced and subjected to both applied and fundamental studies. In the earliest work, reviewed by Faurschou and Knight[1] up to April 1962, laboratory corrosion tests indicated that uranium additions imparted improved resistance to pitting and/or overall corrosion for some ferritic steel types, particularly in acid solutions[1,2].

The present work completes the earlier work on AISI Type 430 stainless steels containing uranium, and similar steels without uranium, by reporting the results of laboratory corrosion tests carried out on these steels during 1962 and 1963. Results are also reported for commercial AISI Type 430 and AISI Type 434 (molybdenum-bearing) stainless steels, in order to provide some basis for a comparison of the effects of uranium and molybdenum.

EXPERIMENTAL

The steels were made at the Physical Metallurgy Division by adding uranium as metal to the aluminum-deoxidized base material in an induction furnace. Each 50-lb furnace charge yielded four steels, i.e. a uranium-free control steel and three steels of differing uranium levels. Compositions of the steels from three 50-lb charges are listed in Table 1.

Subsequent to forging, the steels were annealed for 4 hr at 790°C (1450°F) and then machined into small rectangular coupons for corrosion testing. The coupons were provided with small holes to permit suspension in the test solutions from "Teflon" fluorocarbon resin strips. To ensure surface uniformity, the coupons were lightly ground to a uniform finish on water-cooled, 120-grit silicon-carbide paper. After a measurement of surface area, and weighing, the coupons were degreased in ultrasonically-agitated carbon tetrachloride. The tests were then carried out in glass vessels provided with reflux condensors or tightly fitting lids, to minimize evaporation.

After tests the coupons were rinsed thoroughly, and scrubbed with a light bristle brush. They were then dried, reweighed, and the surfaces examined using a stereo microscope. Typically, adherent deposits were negligible in quantity.

Two 1/8-in.-thick commercial sheet steels, one a standard AISI Type 430 stainless steel, and the other of similar composition but alloyed with 0.76% molybdenum (AISI Type 434), were obtained from Atlas Steels Company, Welland, Ontario (compositions are listed in Table 1). The as-received steels were given the same annealing treatment as the uranium-bearing steels and subsequently handled in the same way during corrosion testing.

RESULTS

The results obtained on the uranium-bearing steels in corrosion tests in five different solutions, in terms of weight losses, appear in Tables 2-5. Representative data for each of the five solutions appear in Figure 1. Some detailed observations on the tests follow.

1. <u>10% Sulphuric Acid and 10% Hydrochloric Acid at 50°C (122°F)</u>
   Subsequent to testing, steels containing 0.18% and 0.41% uranium exhibited generally smoother surfaces and reduced end-grain pitting (Figure 2). Corrosion rates were lowest for the steel with 0.41% uranium (Table 2).

2. Boiling 65% Nitric Acid

Subsequent to testing, steels with 0.5% uranium or less exhibited smooth, dark surfaces similar to the uranium-free steel, while the steels with 1.31% and 2.89% uranium showed noticeably roughened surfaces. From weight loss measurements, uranium additions of 0.18% or less were without effect. An addition of 0.5% uranium appeared to be slightly harmful, while higher levels had a definitely harmful effect (Table 3).

Metallographic sections of these specimens demonstrated a deeply penetrating intergranular attack at the two highest uranium levels. The steel with 0.5% uranium showed a tendency towards increased corrosion at grain boundaries, but the penetrations were relatively shallow. This effect was present but appeared unimportant in the steel with 0.18% uranium.

3. 10.8% Ferric Chloride Hydrate in 0.05% N Hydrochloric Acid, at 23°C (73°F)

This solution has been used to test the pitting susceptibility of stainless steels[3]. Initial tests were carried out on specimens with a non-standard surface, with immersion periods as high as 120 hr. It was found that steady-state corrosion weight losses were 35-55 $mg/cm^2/day$, with no distinct relationship between corrosion rate and uranium level.

Subsequent tests were carried out upon specimens prepared in the standard manner, immersed for shorter periods. After the shortest immersion period there were reduced weight losses for specimens with 0.18% uranium or more, with the lowest weight losses being shown by a specimen with 0.5% uranium (Table 4). Specimens with 0.5% uranium or more exhibited a decreased number of pits. With increasing total immersion time, the results appeared more erratic, and the effect of uranium less definite.

4. Crevice Corrosion in 3% Sodium Chloride Solutions

The tests were carried out at 23°C (73°F), 50°C (122°F) and 80°C (176°F), on single specimens held tightly between glass sheets by rubber bands. At all three temperatures the steels with 0.18% uranium were clearly the most resistant (Table 5), being free from any deep penetrations by corrosion. The steels with 0.5% uranium or more showed a reduced number of deep penetrations. The steel with 0.065% uranium showed somewhat lower weight losses than the uranium-free steels. An indication of the effect of uranium in these tests is given by Figure 4.

5. Microstructure

Uranium is practically insoluble in iron and chromium, and combines chemically with many of the non-metallic elements found in steels. Thus, in the steels under study, uranium would be expected to occur as the intermetallic UFe_2, and as various compounds with oxygen, nitrogen, sulphur and carbon. A detailed study of the microstructure was not undertaken, but polished cross sections of the steels indicated that second-phase particles were more uniformly distributed in the steels with 0.18% and 0.5% uranium, as compared with similar uranium-free steels (Figure 5). At uranium levels greater than 1%, unidentified precipitates, some of which appeared to be the UFe_2-Fe eutectic, became numerous.

6. Effect of Molybdenum

The results obtained in weight-loss corrosion tests on a commercial AISI Type 430 stainless steel and another commercial steel of similar composition containing 0.76% molybdenum (AISI Type 434 stainless steel) appear in Table 6.

The appearance of specimen surfaces after the tests was as follows:

(a) Tests in hydrochloric and sulphuric acids: the molybdenum-containing steel showed reduced end-grain attack, and slightly smoother surfaces.

(b) Tests in nitric acid: after two 48-hr cycles, both steels were similar and showed smooth surfaces.

(c) Tests in acidified ferric chloride: both steels appeared similar and showed deep pits.

(d) Crevice attack in sodium chloride solution: the molybdenum-containing steel generally showed lower weight losses and shallower penetrations by corrosion; however, the deepest single penetration observed was in a specimen of molybdenum-containing steel.

DISCUSSION AND CONCLUSIONS

The main trends in the results are shown in Figure 1, which indicates that uranium additions brought about improved corrosion resistance in four of the test solutions. In 10% H_2SO_4, 10% HCl and acidified 10.8% $FeCl_3$, optimum levels were 0.41% and 0.5% uranium, while in crevice corrosion tests in 3% NaCl solution, the optimum level was 0.18% uranium. In the fifth test solution, boiling 65% nitric acid, there was no benefit from 0.18% uranium or less, and levels higher than 0.18% uranium were increasingly harmful with increasing uranium level.

The results on the commercial AISI Type 430 steels indicated that an addition of 0.76% molybdenum was beneficial in 10% H_2SO_4 and 10% HCl solutions, and, in the crevice corrosion tests, in 3% NaCl solution. However, 0.76% molybdenum did not impart improved corrosion resistance in the acidified 10.8% $FeCl_3$ solution and in boiling 65% nitric acid.

Since only one level of molybdenum was investigated, and since the behaviour of the unalloyed AISI Type 430 stainless steels was different (compare E-6027 with 4803-1 and 4790-1 in 10% HCl), it was not possible to make a direct comparison between molybdenum and uranium. However, there appeared to be some resemblance in the effect of the two additions. Since the beneficial effect of molybdenum on the corrosion of ferritic stainless steel is well known[4,5,6], it appeared that limited field-testing of uranium-bearing AISI Type 430 stainless steel was warranted.

In view of the results reported here, and because other work[1] had established that higher levels of uranium can affect forgeability and impact properties adversely, the practical range of additions to AISI Type 430 stainless steel appeared to be 0.1-0.5% uranium. Accordingly, steels with 0, 0.25 and 0.50% uranium were produced at the Physical Metallurgy Division, rolled, annealed, and fabricated into corrosion specimens. By the summer of 1964, tests were under way as follows:

1. On car bodies, on areas directly exposed to the splashing of water containing de-icing salts in winter (at Ottawa, Halifax, N. S., and Saint John, N. B.).
2. On the roof of the Physical Metallurgy Building in central Ottawa.
3. In sea water, in both the Atlantic Ocean (Halifax, N. S.) and the Pacific Ocean (Esquimalt, B. C.). The racks holding the specimens were constructed so that each specimen contained a crevice.

Preliminary results on these tests should be available within one to three years. It should then be clear whether alloying AISI Type 430 stainless steels with uranium bring about significant improvements in corrosion resistance under service conditions.

ACKNOWLEDGEMENTS

Most of the corrosion testing, and the associated photographic and metallographic work, were performed by J. G. Garrison of the Physical Metallurgy Division. The chemical analyses of the steels were carried out by the Mineral Sciences Division. Some commercial steels were supplied by the Atlas Steels Company, Welland, Ontario.

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TABLE 1

Chemical Analyses of AISI Type 430 Stainless Steels

Heat No.	% U (Total)	% Cr	% C	% Mn	% Si	% S	% P	% Al	% Others
4803-1	0	16.8	0.10	0.80	0.84	0.016	0.018	0.003	-
2	0.017	16.7	0.10	0.77	0.85	0.015	0.018	0.007	-
3	0.065	16.6	0.10	0.77	0.86	0.013	0.018	0.005	-
4	0.18	16.7	0.09	0.77	0.87	0.016	0.018	0.027	-
4790-1	0	17.9	0.09	0.76	1.02	0.011	0.016	0.060	-
2	0.41	17.9	0.09	0.76	0.97	0.012	0.016	0.017	-
3	1.21	17.4	0.10	0.72	0.96	0.012	0.016	0.037	-
4	3.11	17.3	0.08	0.72	0.96	0.011	0.016	0.020	-
4791-5	0	17.6	0.09	0.82	0.96	0.011	0.016	0.021	-
6	0.50	17.6	0.09	0.82	0.93	0.012	0.016	0.013	-
7	1.31	17.5	0.11	0.80	0.92	0.012	0.016	0.028	-
8	2.89	17.2	0.09	0.80	0.94	0.012	0.016	0.074	-
E-6023*	0	17.2	0.13	0.45	0.35	0.020	0.020	0.07	-
E-6027*	0	17.3	0.11	0.43	0.23	0.021	0.021	0.07	0.76% Mo

*From Atlas Steels Company, Welland, Ontario. Heat No. E6027 is AISI Type 434 stainless steel.

TABLE 2

Corrosion in Non-oxidizing Acids at 50°C (122°F)

Heat No.	% Uranium	Weight Losses after 3 hr, mg/cm^2	
		10% HCl	10% H_2SO_4
4803-1	0	49, 68, 57*, 54	62, 75, 86*
4790-1	0	59, 56, 49*	65, 68, 72*
4803-2	0.017	46, 49, 54*, 52	65, 78, 88*
4803-3	0.065	41, 55, 48*, 46	60, 70, 79*
4803-4	0.18	26, 37, 33*, 26	58, 71, 71*
4790-2	0.41	16, 30, 23*	47, 50, 53*
4790-3	1.21	55, 54, 45*	83, 88, 93*
4790-4	3.11	128, 123, 107*	176, 187, 194*

*Argon bubbled into the flasks during testing. For the other tests, oxygen was used.

TABLE 3

Corrosion in Boiling 65% Nitric Acid

Heat No.	% Uranium	Weight Losses, mg/cm^2	
		First Period (0-48 hr)	Second Period (48-96 hr)
4803-1	0	4.7, 3.7	4.2, 4.1
4791-5	0	4.8, 5.0	4.9, 4.8
4803-2	0.017	4.1, 3.8	4.4, 4.3
4803-3	0.065	4.4, 4.1	4.4, 4.5
4803-4	0.18	4.6, 4.2	3.2, 5.9
4791-6	0.50	4.9, 4.9	6.4, 6.7
4791-7	1.31	6.8, 6.7	14, 15
4791-8	2.89	33, 53	86, 110

TABLE 4

Corrosion in Stagnant 10.8% $FeCl_3 \cdot 6H_2O$, 0.05 N HCl Solution at 23°C (73°F)

Heat No.	% Uranium	Weight Losses, mg/cm^2		
		First Period (0-3 hr)	Second Period (3-6 hr)	Third Period (6-9 hr)
4803-1	0	8.5, 8.9	11, 8.4	9.8, 8.9
4791-5	0	8.5, 8.2	12, 8.8	11, 8.5
4803-2	0.017	8.7, 10	11, 11	11, 11
4803-3	0.065	7.6, 8.8	9.5, 9.6	9.4, 8.9
4803-4	0.18	4.8, 5.2	5.4, 5.0	5.7, 6.2
4791-6	0.50	3.5, 3.7	4.4, 3.5	7.9, 3.2
4791-7	1.31	5.2, 5.0	6.1, 4.7	8.2, 4.5
4791-8	2.89	6.7, 6.4	9.5, 6.9	12, 6.8

TABLE 5

Crevice Corrosion in Stirred and Oxygenated 3% NaCl Solution

Heat No.	% Uranium	Weight Loss after 7 Days, mg/cm^2		
		at 23°C (73°F)	at 50°C (122°F)	at 80°C (176°F)
4803-1	0	0.2, 0.2	0.8, 0.9	0.7, 0.7
4791-5	0	0.3, 0.3	1.1, 1.2	0.7, 1.1
4803-2	0.017	0.3, 0.2	0.8, 0.8	0.7, 0.6
4803-3	0.065	0, 0	0.8, 0.5	0.2, 0.5
4803-4	0.18	0, 0	0.1, 0.1	0.1, 0
4791-6	0.50	0.1, 0.1	0.7, 0.4	0.7, 0.3
4791-7	1.31	0.1, 0	0.5, 0.4	0.4, 0.7
4791-8	2.89	0.1, 0.1	0.6, 0.5	0.7, 0.8

TABLE 6

Corrosion Behaviour of AISI Type 430 and Type 434 (0.76% Molybdenum) Stainless Steels

Corrosion Test	Weight Losses, mg/cm^2	
	Heat E-6023	Heat E-6027 (0.76% Mo)
1. 10% hydrochloric acid for 3 hr at 50°C (122°F)	16, 15, 14, 12	10, 10, 10, 9
2. 10% sulphuric acid for 3 hr at 50°C (122°F)	69, 71, 63, 60	47, 48, 41, 39
3. Boiling 65% nitric acid for		
0 - 48 hr	3.0, 2.5	2.4, 2.3
48 - 96 hr	3.6, 3.3	3.5, 3.3
4. 10.8% $FeCl_3 \cdot 6H_2O$, 0.05 N HCl at 23°C (73°F) for		
0 - 3 hr	8.6, 9.3	8.8, 9.5
3 - 6 hr	5.1, 5.7	7.2, 6.4
6 - 9 hr	6.2, 6.5	8.7, 8.1
5. Crevice corrosion after 7 days in 3% NaCl solution at 50°C (122°F)	0.5, 0.5, 0.3, 0.2	0, 0.3, 0.1, 0.2

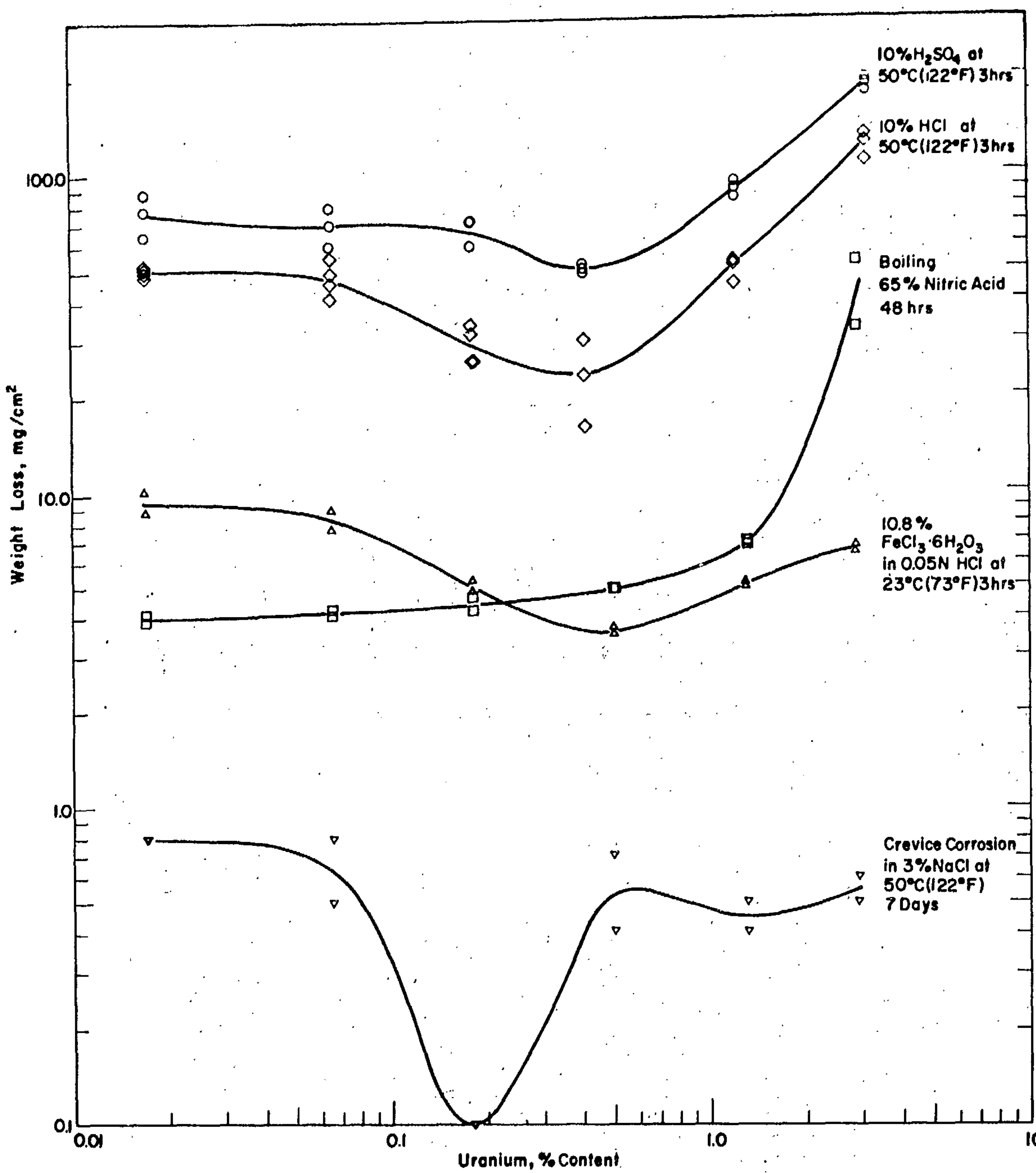
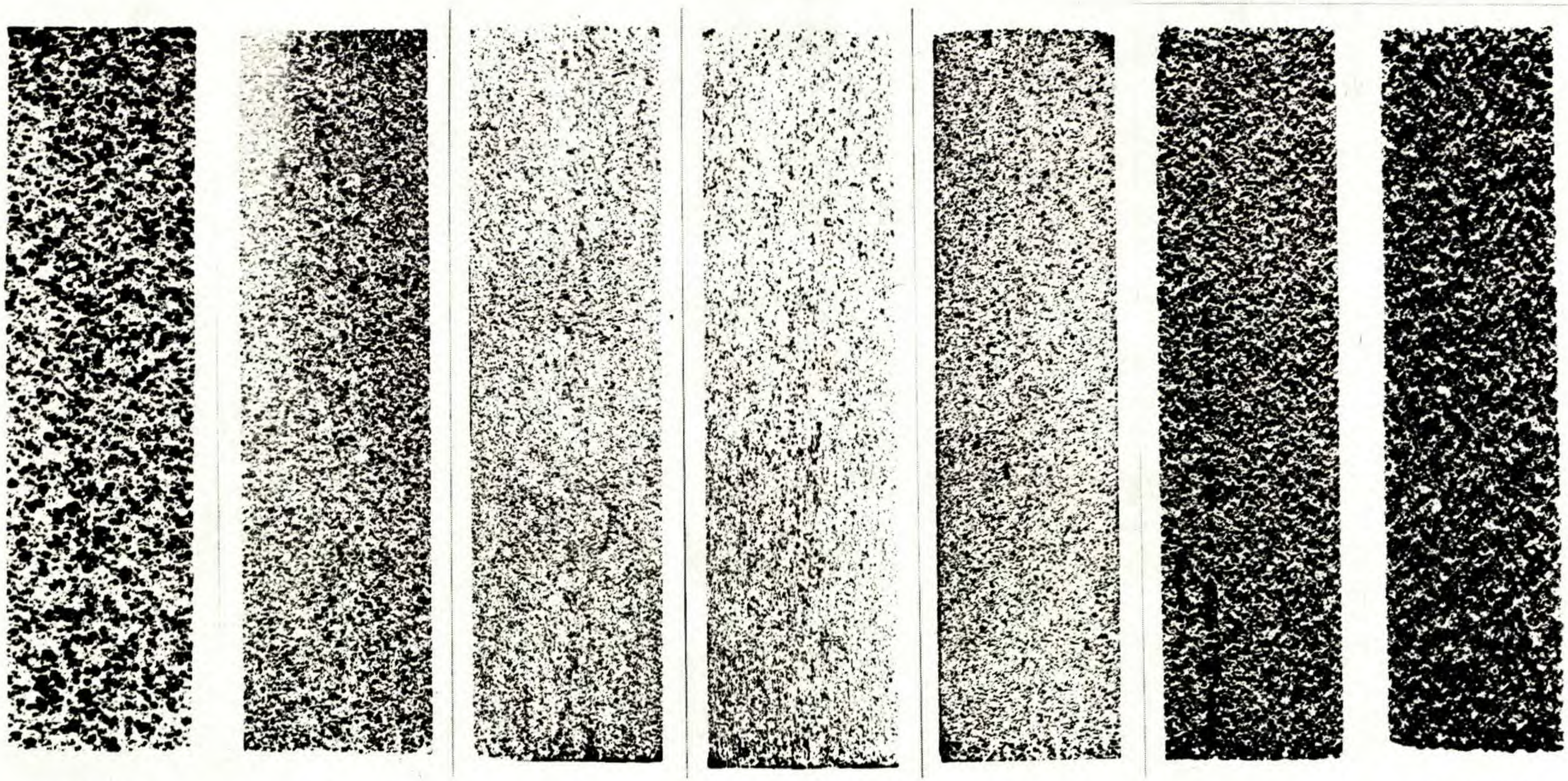
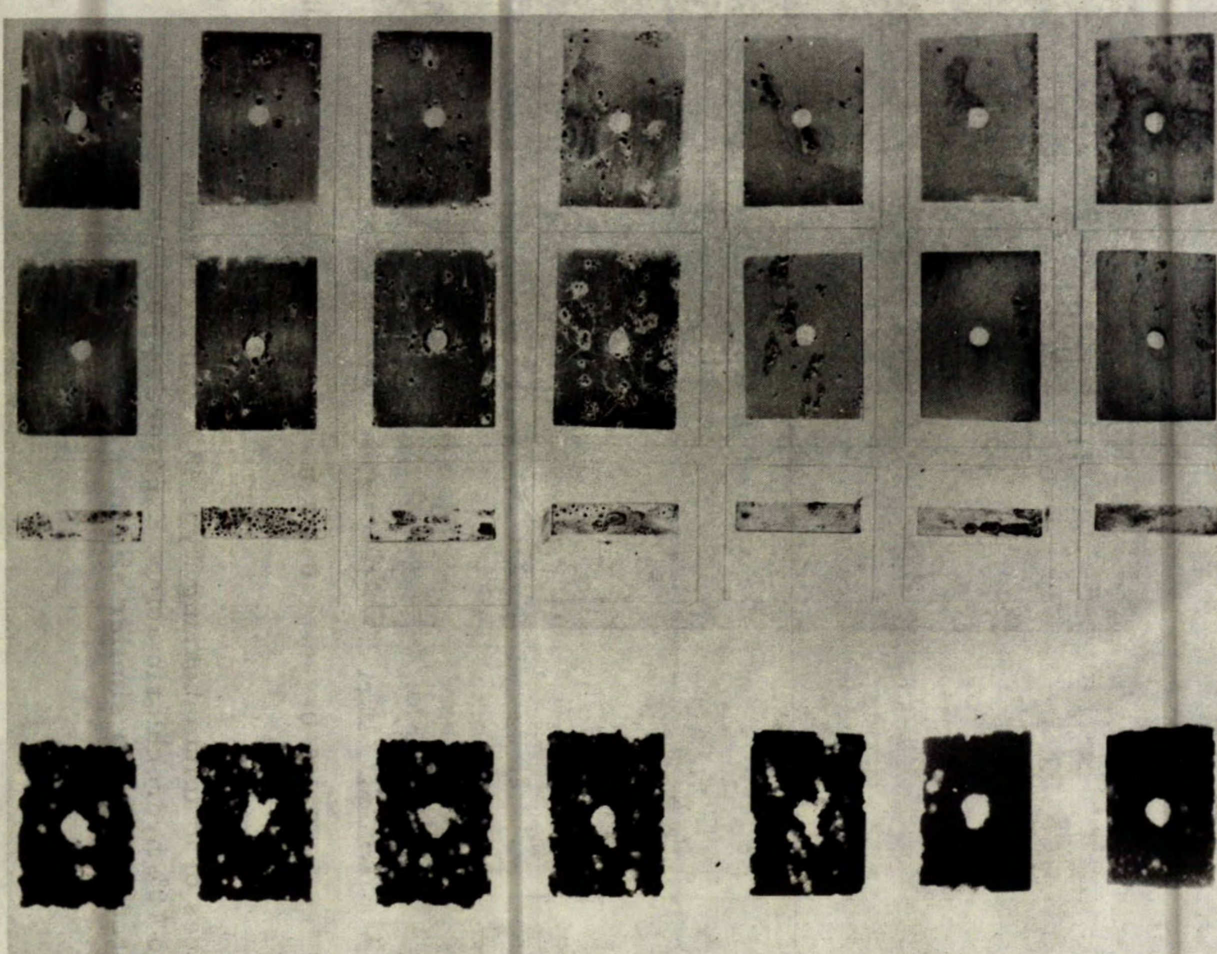


Figure 1. Effect of uranium content on the corrosion of AISI Type 430 stainless steels in various corrosive solutions.



0% U | 0.017% U | 0.065% U | 0.18% U | 0.41% U | 1.21% U | 3.11% U

Figure 2. End-grain surfaces of uranium-bearing Type 430 stainless steels after exposure to 10% hydrochloric acid. Exposure to 10% sulphuric acid brought about a similar effect. X8.

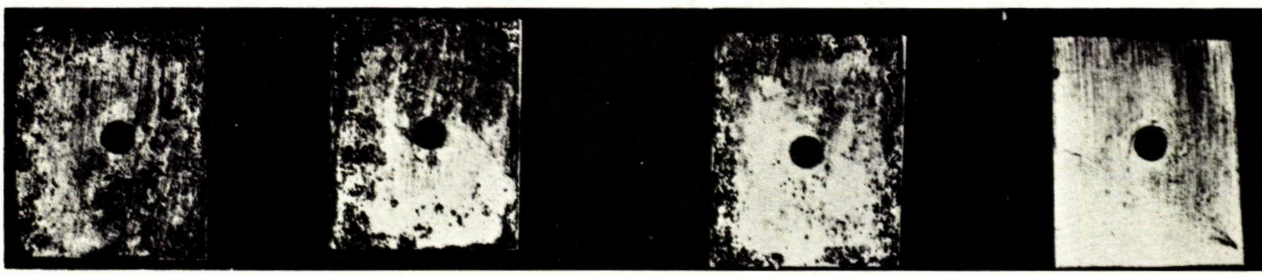


0% U 0.017% U 0.065% U 0.18% U 0.41% U 1.21% U 3.11% U

Figure 3. Pitting corrosion of uranium-bearing Type 430 stainless steels after 24 hr in 10.8% $FeCl_3.6H_2O$, 0.05 N hydrochloric acid at 25°C (77°F).

At the upper part of the figure are macrophotographs of the two major faces and upper edges of the corroded specimens. In the lower part of the figure are X-ray photographs. Loss of metal has occurred at the light areas.

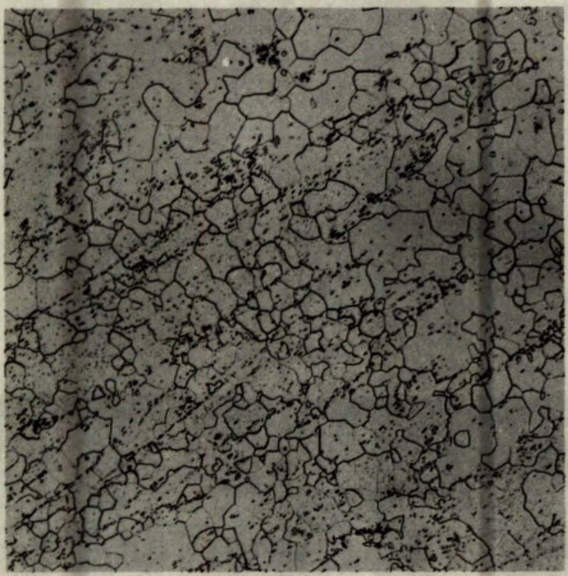
Full scale.



0% U   0.0036% U   0.046% U   0.27% U

Figure 4. Crevice surfaces of uranium-bearing Type 430 stainless steels, after 24 hr in oxygenated 3% sodium chloride solution. The steels shown are from a series reported upon previously[1], but the effect of uranium is typical of the steels in the present work. It should be noted that some of the dark areas, in particular the parallel streaks, are reflections from scratch marks on the abraded metal surfaces. Pits appear as isolated dark patches, predominantly near the edges of the specimens.

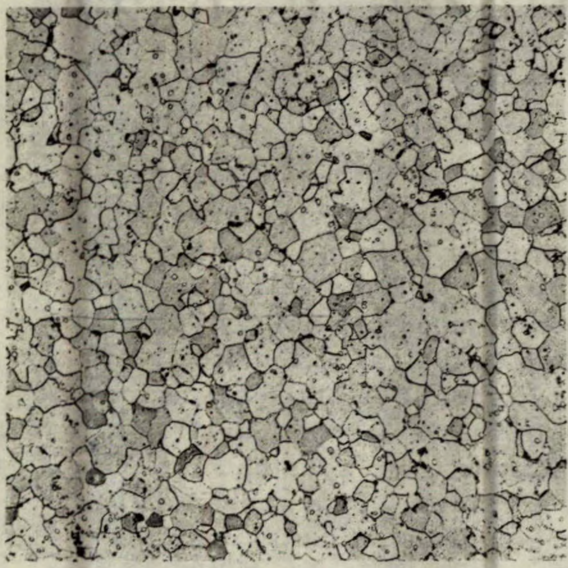
About X2.



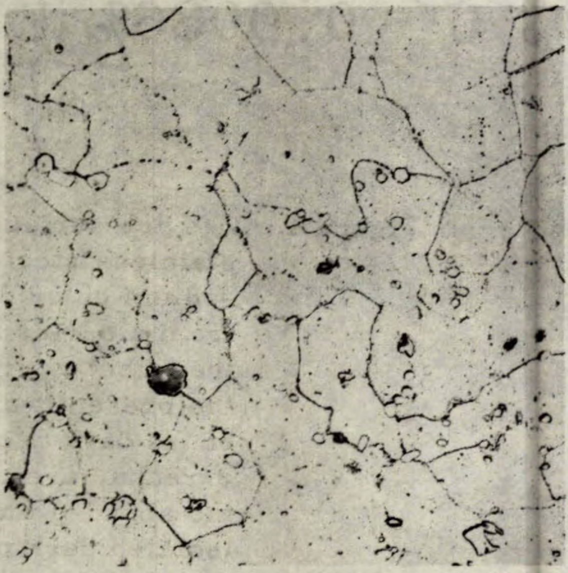
X100

X500

Steel 4791-5 : Uranium-free



X100



X500

Steel 4791-6 : 0.5% uranium

Figure 5. Microstructure of annealed Type 430 stainless steels. Surface preparation: After polishing on parachute cloth with alumina, specimens were etched in Kalling's reagent, then in a modified Carapella reagent.

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