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CORROSION SECTION (M-2)

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* * *

CORROSION TESTING OF TITANIUM-COLUMBIUM ALLOYS
Frederick Nelson, T. W. Binger, Joyce M. Hopkins

June 19, 1945

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SUMMARY

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Problem Under Investigation. Hot rolled and variously heat treated ~~tuballoy-columbium~~ alloys (2, 4, and 6 weight percent ~~columbium~~ ^{NaCl}) were corrosion tested in relatively pure, air-free water, in order to provide part of the information needed to evaluate these alloys as possible slug material.

Important Results. The corrosion resistance, of similarly heat treated alloys in distilled water at 175°C increased with ~~columbium~~ ^{NaCl} content. Heat treatment also had an important effect on corrosion resistance. The alloys which were water quenched from 850°C (gamma range) were most resistant. Similarly heat treated alloys which were also heated 24 hours at 750°C and quenched were somewhat less resistant. The furnace cooled alloys were least resistant and failed rapidly. The water quenched 6 weight percent columbium alloy (1,1) lost 6.5 mg/cm² in a 32.6 day exposure, which is to be compared with a loss of 2450 mg/cm² in one day for tuballoy.

The effects of ~~columbium~~ ^{NaCl} content and of heat treatment on the corrosion resistance of the alloys in boiling, distilled water at 100°C were similar to those at 175°C. This similarity is apparent from weight loss data only for the less resistant alloys (furnace cooled 4 weight percent columbium alloy and all heat treatments of 2 weight percent columbium alloy) which corroded at constant rates. All of the other alloys acquired thin protective oxide films which changed color as corrosion proceeded. Although these alloys corroded at substantially equal rates as judged by weight data, variations in the time required for corresponding colors to appear showed that real differences in corrosion rate occurred. The series of colors produced by interference in the growing oxide films was followed, in some cases, nearly through the second order. The average rate of metal loss from the start of test during a 32 day exposure ranged from 0.0015 to 0.0018 mg/cm²/hr at 100°C.

It is estimated that pimple growth on a leaky, unbonded, canned slug of the most resistant alloy, tested isothermally in water at 100°C, would be about 5 mils in 90 days.

Air free, ~~sodium chloride~~ ^{12% NaCl} (1%) solution attacked the water quenched 6 weight percent ~~columbium~~ ^{NaCl} alloy somewhat more rapidly at 175°C than did distilled water. This alloy was very severely attacked by air-free ~~sodium fluoride~~ ^{12% NaF} (1%) solution at the same temperature.

Aerated water containing mixed electrolytes and a very small concentration of ~~hydrogen peroxide~~ ^{and} attacked the water quenched alloys somewhat faster at 50°C than boiling water did at 100°C, probably as a result of galvanic action.

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Conclusions. Tuballoy-columbium alloys containing 4 to 6 weight percent columbium are unusually resistant to aqueous corrosion when they are properly heat treated. Provided these metastable alloys do not transform to a readily corrodable modification during use, they are (from a corrosion standpoint) much superior to tuballoy for slug material.

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Division Director

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1. INTRODUCTION

Although tuballoy is capable of reacting rapidly with water, it can be used as slug material in a water cooled pile by encasing it in a suitable water-tight jacket. The expected consequences of a defective jacket whereby water can come into contact with the tuballoy are so serious, that it was desired to have a corrosion resistant alloy which could be used instead of tuballoy.

The tuballoy-columbium alloys containing 2 to 6 weight percent columbium were among several groups of alloys proposed for possible use as corrosion-resistant slug material.

The purpose of this investigation was to determine the rate of corrosion by water of variously heat-treated tuballoy-columbium alloys under conditions which approximate those within a leaky, canned slug. Separate studies were undertaken by others with reference to the reactivity of these tuballoy-columbium alloys with hydrogen (CT 5044).

2. MATERIALS TESTED

Tuballoy alloys of 2, 4, and 6 weight percent columbium were prepared for corrosion and metallographic study. Table I gives the history and heat treatments of these alloys along with their chemical analysis. Each alloy, after the rolling operation, was machined to remove any surface imperfections such as folds, and seams. A metallurgical study showed that a very wide range of physical properties was obtainable in these alloys by the various heat treatments.⁽¹⁾

3. METHODS OF CORROSION TESTING

The plan of the corrosion tests was to expose the prepared specimens in water and to determine the weight loss of each after the corrosion product was removed.

Three conditions of exposure were selected. In two of these, the alloys were exposed to water at different temperatures which might occur within a slug. The higher temperature, 178°C, was obtained by open heating of freshly boiled water or salt solution in an autoclave by steam at 125 pounds per square inch pressure. The lower temperature, 100°C, was obtained by actively boiling distilled water at atmospheric pressure. It was anticipated that the effect of temperature on the aqueous corrosion of the alloys could be estimated from the data thus obtained. Because previous work on tuballoy had indicated that dissolved oxygen in distilled water retarded aqueous corrosion, these exposures in air-free water were considered to be conservative with respect to exposure in relatively pure water containing hydrogen peroxide. Near the conclusion of the work, other experiments afforded an opportunity to observe the corrosion of some of the alloys in water at 50°C containing mixed electrolytes, dissolved oxygen, and a very small concentration of hydrogen peroxide.

3.1 Surface Preparation of the Specimens. The samples as received after machining, or after use in a corrosion test, were polished in a hood on various grades of emery paper and finished on No. 1 grit emery paper.

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TABLE I

ALLOYS OF THE TURALLOY-COLUMBIUM SYSTEM

Source Billet No.	Alloy No.	Nom. Wt. % Cb	Chemical Analysis			
			Wt. % Cb			Carbon ave. ppm
			min.	max.	ave.	
C-300	1,3	2	1.60	1.93	1.55	540
	2,3	2				
	3,3	2				
C-301	1,2	4	3.46	3.63	3.57	540
	2,2	4				
	3,2	4				
C-304	1,1	6	6.34	6.61	6.44	550
	2,1	6				
	3,1	6				

History of the Cb alloys:

Billet No. C-300 - 2% Cb, weight 34 lbs, melted in beryllia crucible, cast into 2" diameter silica lined mold. The billet was soaked at 1450°F for 1 hour, rolled into 1/2" diameter rod, air cooled for 10 minutes, water quenched and straightened. Air cooling caused extreme air oxidation.

Billet No. C-301 - 4% Cb, weight 26.8 lbs, melted in a beryllia crucible, cast into a 2" diameter silica lined mold, soaked at 1450°F for 1 hour, rolled into 1/2" rod, air cooled, straightened and centerless ground to 0.401".

Billet No. C-304 - 6% Cb, weight 24.5 lbs, melted in a beryllia crucible, cast into a 2" diameter silica lined mold, soaked at 1450°F for 1 hour, rolled into a 5/8" oval. The billet could not be rolled completely into a 1/2" round, because the bar stuck in the third pass of the 9" mills and became too cool for further rolling.

The rods were cut into 6" lengths and given heat treatments as desired.

Heat treatments (the first number of the alloy number designates heat treatment):

- No. 1 - Alloy heated 2 hours at 850°C, water quenched.
- No. 2 - Alloy heated 2 hours at 850°C, furnace cooled.
- No. 3 - Alloy heated 2 hours at 850°C, water quenched; heated 24 hours at 350°C, water quenched.

One 6" length of each heat treated alloy was available for the water and hydrogen corrosion studies.

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The surface areas were then measured. After the samples were washed thoroughly in acetone to remove grit particles and grease, they were weighed and placed in test. In the autoclave testing surface preparation was done only at the start of a test; between intermediate weighings the samples were not cleaned, but were weighed with adherent corrosion product and then put back in test. In the boiling water test, the samples were surfaced and then exposed continuously for each exposure time shown.

3.2 Autoclave Tests (Water at 178°C). The autoclave test was quite simple. The samples were immersed in freshly boiled distilled water, or other solutions desired, in a 400 ml pyrex beaker covered with a Petri dish, and placed in the autoclave at 125 pounds per square inch steam pressure (178°C). The autoclaves used have large volumes (about 1 to 3 cu ft) so that the partial pressure of the hydrogen gas released in the reaction of the metals with water was minimized. Escape of the hydrogen gas was insured by cracking a steam outlet valve to allow continuous leakage of steam and hydrogen and also by operation of the condensate trap.

Because of the limited supply of each alloy and the lack of suitable standard cleaning procedures at the start of the work, it was decided to record weight changes based on the uncleaned corroded specimens. Weight changes (initial sample weight less the weight of the corroded sample including "adherent" corrosion product, in mg/cm² based on original surface area) were measured at time intervals of 1, 2, 4, 8, 16, 32, and 64 days. At the end of each interval the samples were removed from the test, dried with acetone, weighed and put back in test. Only failures in this test were significant, i.e., the amount of corroded metal exceeded the weight changes based on samples from which the corrosion products were not removed.

A possible interference in the autoclave tests is silica leached from the pyrex beakers during the test (100 to 300 ppm in 4 to 6 days) which may act as an inhibitor and improve the corrosion resistance of some of the alloys or may change the pH of the solution, thereby influencing the rate of metal attack. Vycor beakers were tested and were found to give 50 to 100 ppm silica in 4 to 6 days, which was not a significant improvement.

3.3 Boiling Distilled Water Tests, (100°C). The boiling distilled water tests at about 100°C more nearly approximate slug conditions of corrosion than tests at 178°C and were therefore used in determining most of the corrosion rates of the alloys studied.

The apparatus used in the boiling water test at 100°C consists of a 1500 or 2000 ml pyrex beaker, electric hot plate (550 to 750 watts), capillary jet for feeding distilled water at about 20 ml/min to replace the solution continuously, and glass sample holders. A glass siphon maintains constant water level in the beaker and a varitran is used to control the power output of the heaters. During the test the water boils at all times, thereby minimizing the amount of dissolved gases present.

The interval of exposure in testing ranged from 1 to 64 days. The same specimen was in most cases repolished and used in tests succeeding the one day test, a practice which is not favorable in testing alloys which may be deeply corroded intergranularly or affected in other ways by

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the previous exposure.

Once a specimen had been put in test it was not removed for intermediate weighings, but was removed only at the end of the time interval and then cleaned.

3.4 Water Bath Tests (Water Containing Electrolytes at 50°C). The corrosive effects of hydrogen peroxide and dissolved oxygen in water containing ionic constituents which may be present in slug cooling water were measured for some of the columbium alloys at 50°C. The composition of the water is shown in Table II and detailed information concerning the test is given in CT 3040.

TABLE II

50°C WATER BATH COMPOSITION (AERATED)

Constituent	Desired Strength	Chemical Analysis
Hydrogen peroxide	5×10^{-5} N	1 to 8×10^{-5} N
Iron	0.02 ppm	1.0 2 ppm
Copper	0.01 ppm	0.08 ppm
Manganese	0.01 ppm	-
Sulfate	11.4 ppm	73 to 30 ppm
Aluminum	0.34 ppm	-
Soluble Silica	24.9 ppm	24 to 37 ppm
Calcium	24.0 ppm	23 to 25 ppm
Magnesium	6.1 ppm	6.3 to 9 ppm
Chloride	1.4 ppm	0.8 to 1.4 ppm
Soap Hardness	120.0 ppm	74 to 12 ppm
Total solids	150. ppm	190 to 240 ppm
Bicarbonate	-	35 to 37 ppm
pH	7.85	7.8 ± 0.3
Dissolved oxygen	-	5.4 ppm
Conductivity of feed		3×10^{-4} reciprocal ohms at 50°C

The room temperature water bath solution was fed into a battery jar partially submerged in a 55.0°C thermostatically controlled water bath. The feed solution was aerated at all times, but little agitation of the solution took place in the battery jar where the temperature was 50°C. The specimens were suspended in the corrosive solution by means of glass holders and were cleaned at the end of each test.

3.5 Removal of Corrosion Product. The corrosion product formed in all tests on the more resistant columbium alloys was especially adherent. In order to determine the amount of corroded metal it was necessary to devise cleaning methods which would remove the corrosion product without removing appreciable amounts of the underlying metal. For alloys of low resistance to corrosion in which corrosion product was loose and powdery, cleaning was not so essential; much of the corrosion product sluffed off during the test or could be easily wiped off later to give approximate values of the actual amount of metal lost by corrosion.

The details of the cleaning procedures used are given in the Appendix.

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4. RESULTS AND DISCUSSION

4.1 Autoclave Tests (Water at 178°C). The results of the autoclave tests are given in Table III. It is apparent that the resistance to water corrosion of similarly heat treated alloys increased with columbium content. The improvement due to increasing concentrations of columbium was small in the case of the furnace cooled alloys, all of which corroded rapidly. In the case of the water quenched alloys, however, the 4% alloys were much more resistant than the 2% alloys, and the 6% alloys were definitely the most resistant. At all concentrations of columbium, the water quenched materials were the most corrosion resistant. Their resistance was impaired by reheating 24 hours at 350°C.

The corrosion product formed on the columbium alloys was loose and powdery, except that formed on the water quenched 6% alloys (1,1 and 3,1). These alloys acquired a thin, smooth and adherent dark blue film in the test.

Although it is not the purpose of this work to explain the constitution of the columbium alloys, it appears that furnace cooled alloys contain alpha tuballoy and that the water quenched alloys are chiefly a solid solution of columbium in gamma tuballoy. It is possible that columbium also forms a carbide which is water resistant.

Preliminary tests on "as cast" alloys containing larger amounts of columbium are reported in GT 3043.

4.2 Autoclave Tests (1% Sodium Chloride and 1% Sodium Fluoride Solutions at 178°C). The 1% sodium chloride solution was used to show the corrosive effect due to galvanic action in the presence of a specific ion. Sodium chloride was chosen to make the conducting solution because chloride ion is known to accelerate the aqueous corrosion of many metals, especially the aluminum and iron alloys.

Table IV gives the corrosion rates found in 1% sodium chloride solution at 178°C for the water quenched alloys studied. Comparison with Table III shows that there was a definite but small increase in corrosion due to the presence of sodium chloride. This result is in accord with the low solubility of TuO_2 in hydrochloric acid and the increased conductivity of the solution.

Testing in the 1% sodium fluoride solution, 178°C did show that the corrosion rates of the 6% water quenched alloy and the 4% water quenched alloy (Alloy No. 1,1 and 1,2, respectively) were greatly accelerated by the presence of fluoride ion. In a 48 hour test, the water quenched 6% columbium alloy pitted badly and lost 570 mg/cm² and the 4% water quenched alloy corroded completely. The fluoride probably destroys the protective oxide film, which tends to form in water on the alloy surface, possibly through the formation of a columbium or tuballoy complex.

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TABLE III
TUBALLOY-COLUMBIUM ALLOYS IN WATER HEATED IN STEAM AUTOCLAVE AT 125 psi (178°C)
 Weight change ⁽¹⁾ in mg/cm²

Days in Test	Alloy Numbers									0 % Cb Standard Tuballoy mg/cm ² (2)
	6% Cb (nom.)			4% Cb (nom.)			2% Cb (nom.)			
	1,1	2,1	3,1	1,2	2,2	3,2	1,3	2,3	3,3	
1	-	-335	0.00	-	-451	-0.83	-365	-1060	-357	-2450
2	-0.03	-810	-0.05	-1.06	-	-	-813	-	-920	-
3	-	-1168	-	-	-1385	-3.7	-	-2500	-1529	-
4	0.00	-	-0.2	-3.15	-1776	-5.5	-	-	-	-
8	+0.05	-	-0.23	-18.0	-	-31.9	-	-	-	-
16	+0.21	-	-0.025	-37.6	-	-53.7	-	-	-	-
32	-0.04 (-1.76 based on cleaned speci- mens) (3)	-	-0.03	-35.	-	-	-	-	-	-
62.6	-1.2 (-6.5 cleaned weights) (3)	-	-0.3	-203.	-	-	-	-	-	-

* First number designates heat treatment as follows:

No 1: 2 hrs at 850°C, water quenched.

No.2: 2 hrs at 850°C, furnace cooled.

No.3: 2 hrs at 850°C, water quenched; 24 hours at 350°C, water quenched.

(1) The weight of the corroded specimens included adherent corrosion product. The amount of corroded metal exceeds the weight change shown. Plus means weight gain.

(2) By interpolation of 100°C rate (2.7 mg/cm²/hr) and 183 to 186°C rate (138. mg/cm²/hr).

(3) Corrosion product removed with 40 weight percent nitric acid at 27°C.

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TABLE IV

TURALLOY-COLUMBIUM ALLOYS IN 1% NaCl WATER SOLUTION
AT 178°C (Weight Changes are in mg/cm²)

Days in Test	Alloy Number		
	6% Cb (nom.) 1,1	4% Cb (nom.) 1,2	2% Cb (nom.) 1,3
1	-0.06	-0.55	-497
2	-0.17	-2.5	-950
4	-0.26	-7.2	-1921
8	-0.73	-17.9	-3170
16	-1.61	-43.5	Spec. corroded away
24	-1.96	-	-

Note: The weights of the corroded specimens included adherent corrosion product.

4.3 Boiling Distilled Water (100°C).

(a) Removal of Corrosion Product. It was found that corrosion rates figured from uncleaned sample weights were erratic and sometimes negative due to adherent corrosion product. Table V compares corrosion rates based on cleaned and uncleaned sample weights for the water quenched columbium alloys (heat treatment No. 1) and emphasizes the need for the cleaning of corroded samples.

TABLE V

COMPARISON OF WEIGHT LOSSES DETERMINED FROM CLEANED AND UNCLEARED CORRODED SAMPLES. (3) (Weight loss in mg/cm²)

Days in Test	Cleaned Samples (1)			Uncleaned Samples (2)		
	1,1 6% Cb	1,2 4% Cb	1,3 2% Cb	1,1 6% Cb	1,2 4% Cb	1,3 2% Cb
1	0.35	0.30	0.19	-0.03(4)	-0.01(4)	0.05
2	0.25	0.65	0.31	-0.03(4)	-0.02(4)	0.03
4	0.53	0.63	0.92	0.22	0.05	0.09
8	0.40	0.19	1.41	0.05	0.05	0.04
16	0.77	0.38	3.05	0.09	0.05	0.15
32	1.00	1.14	6.14	0.13	0.32	0.11
64	1.37	0.95	11.43	0.33	0.20	5.0

(1) Weight losses reported are the average of the weight losses given in Table VI-B

(2) The weight losses shown are the weight of initial sample less weight of corroded sample including adherent corrosion product.

(3) Samples exposed in boiling distilled water (100°C)

(4) Weight gain.

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Considerable work was done on the cleaning of the columbium alloys with solutions of nitric acid, because water corroded tuballoy metal was known to clean rapidly to a metallic appearing surface with negligible metal loss in 25 weight percent nitric acid at 26°C. The effectiveness of this method appears to be due, however, to the fact that the corrosion product formed on tuballoy metal, being of a loose porous nature, presents a large area for acid attack. The reaction appears to be concentrated at the interface between the adherent oxide and the uncorroded metal due perhaps to electrochemical differences between tuballoy and its oxide. The method used to clean tuballoy was satisfactory only for cleaning the readily corroded columbium alloys.

A separate cleaning procedure had to be worked out for each alloy composition and heat treatment. Solutions of nitric acid at various concentrations were tried in hopes that the corrosion product would rapidly dissolve from a corroded alloy with negligible metal losses. The reaction of the alloys in nitric acid solutions was followed by determining "cleaning curves", curves in which cumulative weight losses per unit area are plotted against time of exposure in the cleaning solution. When the rate of removal of corrosion product differs to a measurable extent from the rate of metal solution in the cleaning medium, a change of slope is noted in the cleaning curve presumably in the region where the sample becomes clean. In many cases no significant change in slope was found in the curves. The point at which the alloy becomes clean had to be determined by appearance, noting when interference colors disappeared or partially disappeared.

The search for suitable cleaning methods had to be made with samples used in the corrosion tests. This accounts for the variety of cleaning methods used. Details of the cleaning procedures are given in the appendix.

(b) Corrosion Rates. The corrosion rates of the columbium alloys in boiling distilled water are given in Table VI-A for tests lasting up to 64 days. Rates are based on "cleaned weights" of the specimens and are expressed in mg/cm²/hr average metal loss from the start of the test. Table VI-B gives the total metal losses for the alloys in mg/cm² figured from the start of the test.

In the boiling water tests at 100°C, the alloys can be listed in order of decreasing resistance to corrosion, as follows:

Highly Resistant Alloys	Moderately Resistant Alloys	Poorly Resistant Alloys
1,1 1,2 3,1 3,2 2,1*	1,3 3,3	2,2 2,3

*(NOTE: Alloy 2,1 (6 weight percent columbium), furnace cooled, gave low corrosion rates except in the 16 day test for which the corrosion rate was found to be 30 times the expected rate. In this test, deep local corrosion in streaks parallel to the central axis of the cylindrical samples occurred while areas between the corroded sections showed only thin oxide films.

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TABLE VI-A

CORROSION OF TURALLOY-COLUMBIUM ALLOYS IN BOILING WATER AT 100°C
(Average rate of weight loss from start of test, mg/cm²/hr) (1)

No. of Days in Test	6% Cb (nom)			4% Cb (nom)			2% Cb (nom)			0% Cb Standard Tuballoy
	1,1	2,1	3,1	1,2	2,2	3,2	1,3	2,3	3,3	
1	0.016(b) 0.011(a) 0.014(a)	0.091(f) 0.129(f)	0.017(f) 0.011(f)	0.011(a) 0.009(a) 0.018(b)	0.214(b) 0.081(b)	0.021(b)	0.008(a) 0.009(a) 0.007(j)	0.536(j) 0.544(j)	0.009(j) 0.008(j)	2.6 (average of 4 tests)
2	0.004(b) 0.006(b) 0.005(b) 0.006(b)	0.029(f) 0.021(f)	0.008(f) 0.008(f)	0.011(a) 0.011(a) 0.019(b)	0.045(b) 0.140(b)	0.015(f) 0.015(f)	0.035(a) 0.008(a) 0.005(j)	0.447(j) 0.452(j)	0.004(j) 0.004(j)	
4	0.005(b) 0.006(b) -	0.011(f) 0.010(f)	0.006(f) 0.006(f)	0.006(i) 0.006(i) 0.007(b)	0.131(k) 0.096(k)	0.010(f) 0.009(f)	0.008(i) 0.009(i) 0.010(j)	0.474(j) 0.476(j)	0.004(j) 0.003(j)	2.8
8	0.002(c) 0.001(c) 0.003(d)	-	-	0.001(b) 0.001(b)	0.238(b) 0.267(b)	0.005(f) 0.005(f)	0.006(j) 0.009(j) 0.007(j)	0.446(j) 0.450(j)	0.006(j) 0.007(j)	-
16	0.002(e) -	-	0.0025(f)	0.001(b) 0.001(b)	0.195(k) 0.220(k)	0.002(f) 0.003(f)	0.008(j) 0.008(j)	0.547(j) 0.555(j)	0.009(j) 0.007(j)	2.5
32	0.0015(b) 0.0012(f) 0.0012(f)	0.0015(k)	0.0017(f)	0.0016(b) 0.0013(b)	0.095(k)	0.0015(b)	0.008(j)	0.467(j) 0.464(j)	0.007(j)	2.7
48	-	0.0014(m)	0.0014(f)	-	0.178(k)	0.0015(f)	-	-	-	-
64	0.001(g) 0.001(h)	-	-	0.001(g) 0.001(e)	-	-	0.008(j) 0.007(j)	-	0.008(j)	-

(1) Based on original areas of the samples.

Notes: Letters following the corrosion rates refer to cleaning procedure used:

- (a) "Kitchen Cleanser", soft brush.
(b) 30 weight percent HNO₃, 27°C.
(c) 25 weight percent HNO₃, 75°C.
(d) 40 weight percent HNO₃, 25°C.

- (e) 50 weight percent HNO₃, 26°C.
(f) 70 weight percent HNO₃, 26°C.
(g) 40 weight percent HNO₃, 5°C.
(h) 40 weight percent HNO₃, 54°C.

- (i) 25 weight percent HNO₃, 55°C.
(j) 25 wt. percent HNO₃, 27°C.
(k) Conc. H₂SO₄, sat. with MgCl₂.
(m) "Conc." H₂SO₄ with 20 wt. percent HNO₃, 27°C.

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TABLE VI-B

CORROSION OF TURALLOY-COLUMBIUM ALLOYS IN BOILING WATER AT 100°C
 Weight Losses Expressed in mg/cm²

No. of Days in Test	Alloy Number									0% Cb Standard Tuballoy
	6% Cb (nom.)			4% Cb (nom.)			2% Cb (nom.)			
	1,1	2,1	3,1	1,2	2,2	3,2	1,3	2,3	3,3	
1	0.53(b) 0.29(a) 0.37(a)	2.18(f) 3.10(f)	0.40(f) 0.26(g)	0.26(a) 0.22(a) 0.43(b)	5.1(b) 1.9(b) -	0.50(b)	0.19(a) 0.22(a) 0.17(j)	12.34(j) 12.51(j)	0.21(j) 0.18(j)	65 (average of 4 tests)
2	0.19(b) 0.27(b) 0.27(b) 0.29(b)	0.97(f) 1.30(f)	0.36(f) 0.37(f)	0.52(a) 0.52(a) 0.91(b)	2.37(b) 7.24(b)	0.70(f) 0.71(f)	1.65(a) 0.38(a) 0.24(j)	21.05(j) 21.24(j)	0.19(j) 0.19(j)	-
4	0.48(b) 0.58(b) -	1.1(f) 1.0(f)	0.63(f) 0.63(f)	0.58(1) 0.58(1) 0.72(b)	12.58(k) 9.22(k)	0.96(f) 0.86(f)	0.77(1) 0.86(1) 0.93(j)	45.50(j) 45.70(j)	0.53(j) 0.29(j)	274.
8	0.38(c) 0.19(c) 0.58(d)	-	0.47(f) 0.55(f)	0.19(b) 0.19(b)	45.4(b) 52.6(b)	1.0 1.0	1.16(j) 1.73(j) 1.34(j)	85.70(j) 86.35(j)	1.22(j) 1.27(j)	-
16	0.77(e) -	-	0.94(f)	0.58(b) 0.38(b)	75. (k) 85. (k)	1.2(f) 1.2(f)	3.07(j) 3.03(j)	209.0(j) 211.9(j)	3.32(j) 2.33(j)	945.
32	1.15(b) 0.92(f) 0.92(f)	1.15	1.3(f)	1.25(b) 1.04(b)	75.3(k)	1.2(b)	6.14(j)	358.3(j) 356.5(j)	5.19(j)	2210.
48	-	1.6(m)	1.81(f)	-	204. (k)	1.9(f)	-	-	-	-
64	1.40(g) 1.35(h)	-	-	1.2(g) 0.7(e)	-	-	12.27(j) 10.74(j)	-	11.7(j)	-

(1) Based on original areas of the samples.

Note: Letters following the corrosion rates refer to cleaning procedure used:

(a) "Kitchen Cleanser", soft brush.

(b) 30 wt.percent HNO₃, 27°C

(c) 25 wt.percent HNO₃, 75°C

(d) 40 wt.percent HNO₃, 26°C

(e) 50 wt.percent HNO₃, 26°C

(f) 70 wt.percent HNO₃, 26°C

(g) 40 wt.percent HNO₃, 30°C

(h) 40 wt.percent HNO₃, 84°C

(i) 25 wt.percent HNO₃, 65°C

(j) 25 wt.percent HNO₃, 27°C

(k) "Conc." H₂SO₄ sat. with
H₂C₂O₄

(m) "Conc." H₂SO₄ containing
20 wt.percent HNO₃

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These samples had been used in previous tests, etched with 70% nitric acid cleaning procedure, and then hand polished to a metallic surface before the 16 day test. It is thought that the samples may have undergone deep intergranular attack in the nitric acid which was masked by the subsequent hand polishing to a supposedly metallic surface. The surface obtained on etching in 70 weight percent nitric acid was noted to be pyrophoric.))

The highly resistant alloys were observed during corrosion to form thin oxide films which displayed striking interference colors, while the moderately or poorly resistant alloys darkened to give a dull gray or black surface. The thin oxide films formed during the early stages of corrosion appeared to protect the metal from further water attack.

In Figures I-A, I-B, and I-C, metal losses are plotted against time of exposure in 100°C boiling water; the data from which these curves are plotted are found in Table VI-B. The curves indicate that furnace cooled alloys, with the exception of the 6% Cb alloy, show poor resistance to corrosion as compared with the water quenched alloys, (heat treatments Nos. 1 and 3). Columbium in excess of 4% does not appear to enhance the corrosion resistance of the quenched alloys, but markedly influences the resistance to corrosion of the furnace cooled alloys.

The curves also give some indication of the actual corrosion rates of the alloys. Table VII gives the average corrosion rates from the start of the test calculated from the curves of Figure I for 4 and 32 day exposures, together with the slopes of the curves after 8 days exposure.

TABLE VII
CORROSION RATES OF THE TUBALLOY-COLUMBIUM ALLOYS IN
BOILING DISTILLED WATER AT 100°C (mg/cm²/hr)

Alloy No.	Average metal loss from start of test		
	4 days	32 days	slope of curve
1,1*	0.006	0.0013	0.0005
1,2*	0.007	0.0015	0.0005
1,3	0.0076	0.0076	0.0076
3,1*	0.007	0.0017	0.0006
3,2*	0.008	0.0018	0.0006
3,3	0.0075	0.0075	0.0075
2,1*	0.006	0.0014	0.0007
2,2	0.16	0.16	0.16
2,3	0.49	0.49	0.49

* Indicates alloys which displayed interference colors during the test; these alloys showed low corrosion rates which decreased with time indicating that the oxide film formed retarded water corrosion of the alloy.

The values given in Table VII are indicative only of the order of magnitude of the corrosion rates for those alloys in which the total amount of corrosion product is small (0.5 to 2.0 mg/cm²) owing to the difficulty of measuring the actual amount of corrosion product by the cleaning methods used.

FIGURE I-A

CORROSION OF TURALLOY-COLUMBIUM ALLOYS IN BOILING DISTILLED
 WATER (1 Atm.) (Weight Loss After Removal of Corrosion Product)

FIGURE I-2

CORROSION OF TUBALLOY-COLUMBIUM ALLOYS IN BOILING DISTILLED WATER (1 Atm.) (Weight loss after removal of corrosion product).

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FIGURE I-C

CORROSION OF TUBALLOY-COLUMBIUM ALLOYS IN BOILING DISTILLED
WATER (1 Atm.) (weight loss after removal of corrosion product).

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The boiling water tests at 100°C substantiate the results of the autoclave testing in 173°C water in regard to the water quenched alloys (heat treatments Nos. 1 and 3). However in the furnace cooled alloys (heat treatment No. 2), the effect of temperature is more pronounced as the percent columbium is increased. The 6% Cb, furnace cooled alloy (2,1), which withstood water at 100°C very well, did not resist corrosion in water at 173°C.

(e) Interference Colors Observed. The more resistant alloys displayed colors due to light interference at thin oxide films formed by water corrosion. The colors progressed from those of short wave lengths to those of long wave lengths (yellow to dark blue) and showed as many as two orders during the test. Table VIII lists the interference colors observed at various times during continuous exposure of the alloys in 100°C water. Those alloys which did not display interference colors had linear corrosion rates (see Figures I-A, I-B, and I-C). The alloys which did show color changes showed curves which tend to be parabolic, indicating that thin oxide films giving interference colors serve to protect the metal from water corrosion.

The colors of the films observed on the columbium alloys indicate the order of magnitude of corrosion. Theory leads to thicknesses of interference films of the same order of magnitude as the wave length of light.⁽²⁾ Each 1000 Å of film thickness of tuballoy dioxide film corresponds to a corrosion loss of 0.1 mg/cm², assuming a density of 10 for the film material. Table IX gives the time required for the colors of the various alloys to complete the first order color series, and the corresponding metal losses as determined from corrosion rate curves.

TABLE IX

CORROSION WEIGHT LOSSES OF THE Ta-Cb ALLOYS AT END OF THE FIRST ORDER COLOR SERIES. (Samples cleaned of adherent film)

Alloy No.	Nominal Composition	Time to Complete (days)	Total Metal Loss (mg/cm ²)
1,1	6% Cb	18	0.8
1,2	4% Cb	3 to 4	0.7
2,1	6% Cb	16	0.6
3,1	6% Cb	16	0.9
3,2	4% Cb	2 to 3	0.8
			0.76 average

INTERFERENCE COLORS DISPLAYED BY COLUMBIUM-TUBALLOY ALLOYS

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Time	In 100°C Boiling Distilled Water					In 50°C Water Bath Test ^(a)		
	ALLOY NUMBER					ALLOY NUMBER		
	1.1	1.2	2.1	3.1	3.2	1.1	1.2	1.3(c)
1 hour	sl. yellow	yellow	yellow	yellow	yellow brown			
2 hours	yellow	yellow brown	yellow	yellow	dark orange			
3 hours			yellow brown	yellow brown	purple			
4 hours	yellow brown	brownish purple	yellow brown	yellow brown	purple			
5 hours		purple	orange (dark)	orange	purple			
6 hours			orange	orange	blue			
7 hours			orange brown	orange brown	blue			
9 hours			orange brown	orange brown	blue			
17 hours	red brown							
20 hours	purple brown	blue green						
1 day	purple		dark purple	purple	gray green	metallic	metallic	metallic
2 days	bright blue	light green	blue	blue		metallic	yellow	bronze orange
3 days	deep blue	<u>yellow (sl. green)</u>	blue	blue	<u>yellow</u>	yellow	bronze orange	dark orange (c)
4 days	light blue	yellow brown	light blue	light blue	yellow brown	yellow	orange	dark orange
5 days	light blue	yellow brown	light blue	light blue		yellow	orange	dark orange
6 days	light blue	yellow brown	blue green	light blue-green		yellow	orange	dark orange
7 days	light green	orange brown	light green	light green	orange	yellow	orange	brown orange
8 days	light green	orange brown	light green	light green		yellow	red orange	brown orange
9 days	light green	red brown	gray green	gray green	crimson	yellow	purple orange	brown orange
10 days	gray green	red purple			crimson	yellow	red purple	purple
11 days	gray green	purple	sl. green	sl. green	purple	yellow brown	red purple	purple (gray-black)
12 days	gray green	purple	sl. green	sl. green	purple	yellow brown	purple	gray, black, powdery
13 days	sl. green	purple	sl. green	sl. green	purple	yellow brown	purple	gray, black, powdery
14 days	sl. green	purple	sl. green	sl. green	blue purple	yellow brown	purple	gray, black, powdery
15 days	sl. green	purple	sl. green	sl. green	blue purple	orange	bluish purple	gray, black, powdery
16 days	sl. green	purple blue	<u>metallic (sl.g.)</u>	<u>metallic (sl.g.)</u>	blue	orange	bluish purple	Sample covered with loose gray product; considerable pitting was noted on removal of corrosion product after 29 days exposure. Blue-black color was noted under corrosion product excepting where sample was pitted.
17 days	sl. green	deep blue			deep blue	orange	bluish purple	
18 days	<u>metallic (b)</u>	deep blue			deep green (sl.b.)	orange	bluish purple	
19 days	metallic	deep blue				orange	bluish purple	
20 days	metallic	deep blue			deep green	orange	bluish purple	
21 days	metallic	deep blue-green			deep green	orange	blue	
21-24 days	metallic					orange	blue	
25-29 days	metallic (sl.y.)					orange	blue	
34 days	yellow					orange	blue	
39-41 days	yellow brown			orange pink (39da.)				
42 days	l. orange-brown							
43 days	l. orange-brown							
44-47 days	orange brown		dark orange pink (44 days)	orange pink (44da.)				
48 days	bright orange							
55 days	bright orange							
56 days	orange							
63 days	orange pink							
64 days	red brown							

1,3; 2,2; 2,3; 3,3 do not show color changes in 100°C test, they became gray or black and corroded at constant rate.

(a) See CT 3040.

(b) Underscoring indicates time where second order colors begin to form.

(c) Alloy 1,3 began to form a gray black product after 4 days which finally covered the entire sample in about 12 days.

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(d) Pimple Formation in Canned Slugs. Leaky, aluminum canned, unbonded tuballoy slugs are known to pimple rapidly in water. Tuballoy hydride is formed initially in the pimples by reaction of the metal with hydrogen released within the can at another part of the slug as a result of oxidation of tuballoy by water. The hydride reaction takes place at active spots in the slug metal rather than uniformly over the surface. Previous work with canned tuballoy slugs showed that when one mil of tuballoy is converted by water to oxide, the observed radial swelling is 3.5 mils. If it is assumed that compacted hydride has the same density as compacted oxide, the swelling at the localized sites of hydride formation is accounted for by the replacement of one volume of metal with 4.5 volumes of packed hydride.

It was of interest to estimate the speed of pimple formation on leaky, aluminum canned, unbonded slugs of tuballoy-columbium alloy. The measured corrosion rates of the columbium alloys in boiling distilled water make possible an estimate of the rate of hydrogen liberation within the can. Assuming that hydrogen from 25 cm² of slug surface reacting with water reaches 1 cm² of slug surface to form a pimple of uniform height, the swelling corresponding to a water corrosion rate of 0.001 mg Tu/cm²/hr is 3.9 mils in 90 days. This factor and the average rate of metal loss during 32 days exposure in boiling distilled water at 100°C shown in Table VII give a conservative estimate of swelling to be expected at 90 days, as shown in Table X.

TABLE X

ESTIMATED PIMPLE HEIGHT ON LEAKY, UNBONDED TUBALLOY-COLUMBIUM SLUGS (After 90 Days Exposure at 100°C)

Alloy Number	1,1	2,1	3,1	1,2	2,2	3,2	1,3	2,3	3,3
Weight Percent Cb	6	6	6	4	4	4	2	2	2
Pimple Height in mils	5.1	5.5	6.6	5.9	620	7.0	30	1900	29

It is seen that only two of the alloys are estimated to swell more than the maximum diameter tolerance of 80 mils. This estimate does not allow, however, for the expected rise of the slug surface temperature due to accumulation of corrosion product within the aluminum can. Neither does it allow for any transformation of the metastable quenched alloys to a more rapidly corroded modification during operation. Experimental data, especially with reference to the latter effect, are needed as the next step in evaluating the columbium alloys as slug materials from a corrosion standpoint.

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4.4 Water Bath Tests (Water Containing Electrolytes at 50°C)

(a) Corrosion Rates. Table XI gives the weight losses found for several of the columbium alloys in aerated water containing a very small concentration of hydrogen peroxide in addition to electrolytes such as might occur in a ground water.

TABLE XI

CORROSION OF TUBALLOY-COLUMBIUM ALLOYS IN AERATED
WATER CONTAINING ELECTROLYTES AT 50°C
(Weight losses based on cleaned samples)

Alloy Number and Composition	50°C Water Bath 29 days exposure		100°C Distilled Water 32 days exposure	
	Average weight loss		Average weight loss	
	(mg/cm ²)	(mg/cm ² /hr)	(mg/cm ²)	(mg/cm ² /hr)
1,1 (6% Cb)	0.96	0.0015	1.15	0.0015
	0.64	0.0009	0.92	0.0012
	-	-	0.92	0.0012
1,2 (4% Cb)	1.5	0.0021	1.23	0.0016
	1.8	0.0026	1.04	0.0015
1,3 (2% Cb)	12.7	0.018	6.14	0.008
	11.6	0.016	-	-
Standard Tuballoy	74	0.10	2210.	2.7
	162	0.23	-	-
	42	0.06	-	-

The corrosion of the water quenched tuballoy-columbium alloys at 50°C in aerated water containing electrolytes increased as the columbium content decreased. The same relation was found for the relative corrosion rates of these alloys in boiling distilled water at 100°C. Alloy 1,3 was attacked more in the aerated water containing electrolytes, relative to the other alloys, than it was in the boiling distilled water. This probably was the result of breakdown of the protective oxide film, described in Table VIII, and galvanic action in the electrolyte.

Standard tuballoy was attacked far more in boiling distilled water, relative to the alloys, than it was in the aerated electrolyte. The oxide formed on standard tuballoy in boiling distilled water was not adherent, while that formed in the aerated electrolyte was very thin and adherent over a part of the surface. Barnacles of oxide formed, however, at other parts of the surface which probably were anodic to the surface protected with an oxide film. This pitting action accounts for the high corrosion of standard tuballoy in aerated electrolyte at 50°C relative to that in aerated, distilled water at 50°C where pitting did not occur. In the latter case the samples were covered with a thin,

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smooth, dark blue film. The weight loss due to a 34 day exposure in aerated distilled water at 50°C was 0.41 mg/cm² and the average rate of metal loss from the start of the test was 0.001 mg/cm²/hr. (CT 5055).

(b) Interference Colors Observed. The interference colors which the alloys display in the 50°C water bath tests are shown in Table VIII along with the color changes noted for the alloys in the 100°C distilled water tests.

Corrosion in the initial stages of the test is much slower in the 50°C water bath than in the 100°C distilled water as is evidenced by the absence of interference colors during the first 24 hours in the 50°C water bath.

Alloy 1,1 (8 wt.% Cb) changes from metallic to yellow to orange and does not completely show the first order color series; alloy 1,2 (4 wt.% Cb) changes from metallic to yellow and finally to blue without showing evidence of second order colors. The large corrosion weight losses in the 1,2 alloy determined on removing the corrosion product (1.5 and 1.8 mg/cm²) suggest that second order colors should have appeared. Graveling in the film may have occurred to account for their absence.

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5. APPENDIX

5.1 Cleaning Procedures Used in Removing Corrosion Product.

Solutions of nitric acid at various temperatures and concentrations have been used on the water corroded alloys to remove adherent corrosion product. It was hoped that the corrosion product would have a high rate of removal as compared with the rate of solution of the unaltered metal. In the case of water corroded tuballoy, the corroded samples cleaned rapidly to a metallic appearing surface in about 5 minutes with negligible losses of metal in 25 weight percent nitric acid at 26°C. "Cleaning curves", curves in which cumulative weight losses of the corroded sample are plotted against time of exposure in the cleaning solution showed a drastic change in slope in the region where the sample became metallic.

In general, the columbium alloys which had a low resistance to corrosion by water behaved like tuballoy in dilute nitric acid to enable accurate estimates of the weight of the corrosion product. Those alloys which had a superior resistance to water corrosion, i.e., in which the corrosion product consisted of a thin oxide film which displayed interference colors and was small in amount, could not be cleaned with a high degree of accuracy in the same solution. Cleaning curves showed only slight slope changes or were linear and the point at which a sample became clean had to be based mainly on appearance by noting the disappearance of interference colors.

The cleaning of the columbium alloys to remove corrosion product can be considered under two heads, as follows:

- (1) Accurately cleaned alloys (alloys of low corrosion resistance).
- (2) Difficultly cleaned alloys (alloys of high corrosion resistance).

(a) Cleaning of Alloys of Low Corrosion Resistance. All of the 2 weight percent columbium alloys (1,3, 2,3, 3,3) cleaned accurately in 25 weight percent nitric acid to give curves of the type shown in Figure II. The minimum value for the weight loss of metal due to corrosion is taken as the intersection of the ordinate with the best straight line drawn through the "leveling out" part of the curve; the maximum value is taken at the point on the curve where the sample first appears practically all metallic. The accuracy of the method in cleaning the 2 weight percent alloys is estimated to be 0.1 mg/cm^2 of the total weight loss of metal due to corrosion.

The furnace cooled 4 weight percent columbium alloy cleaned in 30 weight percent nitric acid at 27°C to leave a dull, semi-metallic appearing surface and gave curves of the type shown in Figure III. The weight losses reported for the 4 weight percent furnace cooled columbium alloys cleaned by this method are estimated to be accurate within 0.5 mg/cm^2 .

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FIGURE II

CLEANING OF 1,3 ALLOY IN 25 WEIGHT PERCENT HNO_3 at 27°C

CLEANING OF ALLOY 2,2 IN 30 WEIGHT PERCENT HNO_3
at 27°C

(b) Cleaning of Alloys of High Corrosion Resistance. These corroded alloys displayed interference colors which gradually disappeared on dipping in nitric acid solution. In the nitric acid the corroded sample showed a series of colors which progressed in the reverse order of the color changes noted during the corrosion of the alloys. Inflections in the cleaning curve in the region where the sample began to appear metallic gave limits for the value of the weight loss in the sample due to corrosion. The best straight line was drawn through the "leveling out" part of the curve (where a nearly constant slope is obtained presumably due to the exposure of a homogeneous, metallic surface) to intersect the ordinate at a point giving a minimum value of the weight loss in the specimen. A maximum value is taken at the point on the curve where the sample first appears to be practically all metallic. Figure IV shows the type of curves obtained for a corroded alloy and a metallic (hand polished on No. 1 grit emery paper) specimen of the same alloy.

In some alloys an increase in slope was observed at the region where the sample became cleaned to a metallic surface and gave curves of the type shown in Figures V and VI. In this type of curve the value reported for the weight loss in the sample is taken as the intersection of the best straight line through the points on the curve where the sample appears metallic with the best straight line drawn through points on the curve where no metallic surface was noted.

Table XII lists the cleaning procedures used for the various alloys, giving figure numbers of typical cleaning curves, and the accuracy of each procedure in determining the weight loss of metal from samples corroded in distilled water at 100°C for 1 and 64 days.

The accuracy of the cleaning methods are rather poor due to the small metal losses by corrosion of the resistant alloys in boiling distilled water, (1 to 2 mg/cm²). As the amount of corrosion in an alloy increases, of course, the accuracy of the methods increase. A 5 weight percent alloy, water quenched from 850°C, corroded in distilled water at 178°C gave a cleaning curve as shown in Figure VII. The metal loss in the alloy due to corrosion was found to be 6.5 ± 0.4 which corresponds to an estimated accuracy of about 10 percent.

The cleaning curves of those alloys in which no significant inflection in the curve was obtained are represented by the straight line curve shown in Figure VIII. The value reported for the metal loss in the specimen due to water corrosion is determined from the point on the curve where the sample becomes practically all metallic or shows only traces of interference colors. Metal losses determined on this basis are likely to be larger than actual losses.

TABLE XII

REMOVAL OF CORROSION PRODUCT FROM ALLOYS CORRODED IN BOILING
DISTILLED WATER

Alloy No.	Cleaning Solution		Fig. No. of Clean- ing Curve	Estimated		Best method of those tried
	Wt. percent Nitric Acid	Temp. °C		1 day rate percent	64 day rate percent	
1,1	70	26	VII	50	25 to 50	Best
	40	26	IV	50	25 to 50	
	30	26	Note 1	50	25 to 50	
	40	3	Note 1	50	25 to 50	
	10	84	Note 1	50	25 to 50	
1,2	50	26	V	40	25	Best
	30	27	Note 1	40	25	
	40	3	Note 1	40	25	
3,1	70	26	Note 1	40	25 to 40	Best
3,2	70	26	VI	50	25	Best
	30	27	Like V	50	25	
2,1	70	26	Note 2	50	50	Best
	20(1)	26	Note 3	50	25 to 50	

(1) 20 weight percent nitric with 75 weight percent sulfuric acid.

NOTE 1: Cleaning curves do not show significant changes in slope where sample becomes metallic. The point where interference colors disappear to give a metallic appearing surface is used to determine a maximum value for the corrosion weight loss; a minimum value is obtained from a point where the sample still shows considerable interference colors.

NOTE 2: Interference colors disappear but the nitric acid darkens the underlying metal, making identification of the point at which the corrosion film is removed difficult.

NOTE 3: The solution, 20 weight percent nitric with 75 weight percent sulfuric acid removes interference colored films to leave a metallic appearing specimen. The cleaning curve does not show a change in slope in the region where the specimen becomes clean.

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Weight loss mg/cm^2 , based on initial sample weight.

FIGURE IV

CLEANING OF TUBALLOY-COLUMBIUM ALLOY 1,1 in 40 WEIGHT PERCENT HNO_3 , 26°C

30 FIGURE V

CLEANING WATER CORRODED 1,2 ALLOY IN 50 WEIGHT
PERCENT HNO_3 , 26°C

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FIGURE VI

CLEANING ALLOY 3,2 in 70 WEIGHT PERCENT HNO_3 , at 26°C

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FIGURE VII

CLEANING OF ALLOY 1.1 in 40 WEIGHT PERCENT HNO_3 , 26°C

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Weight loss mg/cm^2 , based on initial sample weight

FIGURE VIII

CLEANING OF ALLOY 1.1 in 70 WEIGHT PERCENT HNO_3 , at 26°C

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5.2 Photomicrographs

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Figure IX

500 X

Alloy 1,2: Water Quenched
from 850°C

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Figure X

500X

Alloy 3,2: Water Quenched
from 850°C; Tempered 24 hours at 350°C
and Water Quenched

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Figure XI

500 X

Alloy 2,2: Furnace Cooled

MICROSTRUCTURES OF THE 4 NOMINAL WEIGHT PERCENT TUBALLOY-COLUMBIUM ALLOYS.
Etched with H_3PO_4 , Ethyl Glycol, Absolute Alcohol (5 : 5 : 8 by volume).

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Figure XII
Alloy 3,2 after 20 days in
boiling, distilled water.
(deep green)

Figure XIII
Alloy 1,2 exposed in boiling,
distilled water.
(left) 7 days orange-brown
11 days purple
3 days yellow
(Right) 9 days red-brown

Figure XIV
Alloy 1,1 exposed 3 days in
boiling, distilled water.
(deep blue)

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