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Metallurgy Division

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CORROSION OF TUBALLOY-MOLYBDENUM ALLOYS BY WATER

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SUMMARY

A series of hot-rolled ⁷¹~~tuballoy~~ alloys containing nominally 5% molybdenum by weight were tested in water heated in the autoclave by 125 ^{psi} pounds per square inch steam pressure (178°C). The alloys were also tested in boiling water at atmospheric pressure to measure resistance to corrosion by distilled water which is essentially free of dissolved gases. The water-quenched and annealed alloys were more corrosion resistant than the alloys which were only water quenched or those which were furnace cooled. The furnace-cooled alloys cracked in test. The alloys which were melted in ^{BeO}~~beryllia~~ crucibles showed slightly more corrosion resistance than the alloys melted in graphite crucibles. The most corrosion resistant alloy (Alloy 3.4) tested in boiling distilled water at 100°C corroded at the average rate of 0.02 mg/cm²/hr. Standard ~~tuballoy~~ corrodes approximately 135 times more rapidly under the same conditions. (auth)

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1. INTRODUCTION

The primary purpose of the corrosion work was to find a tuballoy alloy which would be sufficiently corrosion resistant to be useful for canned slugs even if some of the cans were to leak. The secondary purpose was to obtain general corrosion data on tuballoy alloys.

The alloys were tested in the steam autoclave and in boiling water beaker tests. The autoclave test was planned as a screening test to permit rapid classification of the alloys. The boiling water beaker test was intended to more nearly approximate slug conditions. In use, the canned slug is exposed to water of about 70°C. Water within a leaky slug would quickly become hydrogen saturated. There is evidence to indicate that the corrosion of tuballoy in hydrogen saturated water is similar to its corrosion in water free of dissolved gases. The boiling water beaker test, which provided exposure of the specimens to water free of dissolved gases at 100°C, approximated slug conditions.

2. MATERIALS TESTED

The series of tuballoy-molybdenum alloys tested consisted of six alloys. The alloys were numbered as follows: 1,4, 1,5, 2,4, 2,5, 3,4, and 3,5. The first number refers to the heat treatment which the alloy received. Heat treatments are as follows:

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

The second number refers to the kind of crucible in which the alloy was melted and are as follows:

- No.4: BeO Crucible.
- No.5: Graphite Crucible.

All the alloys contained nominally 5% molybdenum by weight. Actual chemical analysis showed the following results:

	<u>Alloys melted in BeO Crucibles</u>	<u>Alloys melted in graphite Crucibles</u>
Molybdenum	4.6 weight percent	4.4 weight percent
Carbon	640 to 790 ppm	760 to 900 ppm
Oxygen	60±12 ppm	13±2 ppm
Beryllium	100 ppm	2 to 75 ppm

The samples were made from a billet which was hot rolled into a 1/2 inch diameter rod and then cut down to a 3/8 inch diameter rod in order to insure freedom from surface defects.

A sample of each kind of these alloys was sent for a metallographic study. The structure of the uncorroded metal shown in Figure I was typical

of all samples. In sections taken parallel to the rolling direction, the finely divided constituents were aligned in the rolling direction. The alloys melted in BeO crucibles showed less than 5 percent porous area, but considerably more than the alloys melted in graphite.

3. AUTOCLAVE TESTING

3.1 Course Pursued in Study. Due to the increasing number of alloys developed in the hope of finding a tuballoy alloy which would be resistant to aqueous corrosion, it became necessary to develop a screening test to eliminate quickly the alloys with a low resistance to corrosion. It was decided that any alloy which did not corrode rapidly in this accelerated test would be studied further under conditions which more nearly simulated those in a leaky slug.

The autoclave screening test was very simple. Each specimen was weighed and then immersed in boiled distilled water in a 400cc pyrex glass beaker covered with a Petri dish, and placed in the autoclave at 125 pounds per square inch steam pressure (178°C).

Each specimen was given a standard surface preparation before being placed in test. It was ground on various grades of emery paper and finished on No. 1 grit paper. The surface area was measured and the specimen was washed thoroughly with C.P. acetone to remove any emery particles and grease.

It was decided to record weight changes (in mg/cm² based on original surface area) at regular time intervals of 1, 2, 4, 8, 16, and 32 days and this schedule was followed as closely as possible.

Because of the limited supply of each alloy and the lack of dependable procedures to remove the corrosion product, it was decided to record weight changes based on uncleaned specimens. At the specified time intervals, the specimens were removed from test, dried with acetone, weighed, and placed back in test. This procedure obviously does not yield accurate results, but it must be remembered that this test was intended to eliminate the readily corroded materials. The actual amount of altered metal exceeded the weight changes reported.

Another point which should be mentioned is the fact that water leaches silica from pyrex beakers at this temperature. It is possible that this silica (100 to 300 ppm in 4 to 6 days) may act as an inhibitor and improve the resistance to corrosion of some of the alloys. Any protective effect of silica would merely tend to increase the number of alloys chosen for subsequent tests. In trying to overcome this difficulty Vycor beakers were tried, and the silica content was decreased to 50 to 100 ppm in 4 to 6 days which is not sufficient improvement. For future work of this type it would be well to try beakers made of plastic, or platinum with the specimen suspended so there is no metal-to-metal contact, or crucibles made of TiO2.

3.2 Data and Calculated Results. The results of the autoclave testing of this series of molybdenum alloys are given in Table I. The values are average weight losses from the start of the test given in mg/cm² based on original surface area and on the uncleaned corroded specimen. It should be

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FIGURE I

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STRUCTURE OF ALLOY 2,5 AFTER EXPOSURE IN BOILING
DISTILLED WATER AT 100°C FOR 8 DAYS, SHOWING
SMALL CRACKS

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noted that in cases where the specimen completely corroded away, the weight loss as given in mg/cm^2 is limited by the initial weight and area of the specimen, and is not necessarily comparable to the other results.

TABLE I

CORROSION OF Tu/Mo ALLOYS IN WATER HEATED IN AUTOCLAVE (178°)
Average weight loss in mg/cm^2 based on original areas

Days in Test	5% Mo Alloys Melted in BeO Crucibles			5% Mo Alloys Melted in Graphite Crucibles		
	Alloy Number			Alloy Number		
	1,4	2,4	3,4	1,5	2,5	3,5
1	581	549	177	665	433	289
2	1014	-	-	1150	-	-
3	-	3910(1)	541	1620(2)	4350(1)	2730(3)
4	-	-	710	-	-	-
8	-	-	1263	-	-	-
16	-	-	2240	-	-	-

- (1) Specimen corroded away.
(2) 1623 based on cleaned specimen.
(3) Specimen cracked.

The only specimen which was observed to crack was alloy 3,5 after a 3 day test. In the case of the furnace cooled alloys which corroded away after a 3 day test, it is probable that the specimens cracked at some time between 1 and 3 days before falling apart. The probable effect of cracks in a specimen would be to decrease the actual weight loss during the early part of the exposure because the cracks would retain corrosion product.

3.3 Conclusions. These tuballoy-molybdenum alloys are not very resistant to corrosion. The best alloy tested (alloy 3,4) corroded in water heated in the steam autoclave at the average rate of about 7 to 8 $\text{mg}/\text{cm}^2/\text{hr}$, while tuballoy corrodes approximately sixteen times more rapidly under these conditions.

On the basis of the data in Table I, it appears that the alloys with a No. 3 heat treatment are the most resistant to corrosion, and those with a No. 1 heat treatment are the least resistant. It also appears that the alloys melted in BeO crucibles may be slightly superior to those melted in graphite crucibles.

3.4 Discussion. The type of crucible used for melting and the type of heat treatment makes no practical difference in the corrosion of the alloys since all corrode at a very high rate and within the same approximate range. The experimental error involved is too great to warrant drawing any close distinctions.

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There was some question as to whether or not the samples might have been mixed since a different effect of heat treatment was found in the tuballoy-molybdenum alloys than was found in tuballoy-columbium alloys similarly heat treated. Therefore one sample of each heat treatment of the tuballoy-molybdenum alloys was given a Rockwell hardness test. The results checked very closely with the hardness data given in CT 2794, p.21; thus, the samples could not have been interchanged.

4. BOILING WATER BEAKER TESTS

4.1 Course Pursued in Study. The boiling water beaker test apparatus consists of a beaker (1500cc or 2000cc) filled with distilled water which is actively boiled on an electric hot plate with 550 watts input. The distilled water is replenished in each beaker by means of a capillary tube calibrated to deliver approximately 20 cc/min. The distilled water line comes directly from the still and contains a float valve which maintains the constant head necessary for the capillary to deliver the calibrated amount. A constant water level is maintained in the beaker by a glass siphon which dips in the side of the beaker and carries excess water into the drain. The samples are hung over the side of the beaker in glass holders which reach about two-thirds of the way to the bottom of the beaker.

The samples are given a standard preparation before being placed in test. After they are machined, they are polished on No. 1 grit emery paper, and the surface areas are measured. They are then washed with C.P. acetone to remove grease and loose particles of metal or emery paper, and are weighed. They are plated in glass holders by means of cork-tipped forceps and immersed in the beakers of boiling water.

The general plan followed with regard to length of tests was to run 1, 2, 4, 8, 16, and 32 day tests for each type of alloy. The samples were not removed from the water for drying, weighing, and returning to test at any intermediate time during a test. Thus, irreversible changes in the film of corrosion product due to dehydration were avoided.

At the end of each test, the sample was removed from the water and cooled. It was given an acetone dip, or it was washed in water, wiped, and then dipped in acetone if the corrosion product was loose and crumbling from the sample. The sample was weighed to determine the weight change during test before cleaning. Next, the sample was cleaned chemically in order to remove the products of corrosion.

4.2 Reason for Cleaning Samples. When a weighed metallic sample is exposed in boiling distilled water, a certain amount of metal is converted to "corrosion product" which is largely an oxide. The object of the test is to measure the amount of the changed metal. If the sample is weighed on removal from test without cleaning, the measured loss is not the total metal loss since some "corrosion product" adheres to the sample. The amount which adheres cannot ordinarily be estimated since it varies depending on the alloy and on the length of test.

In short tests where the amount of corrosion is small, practically all the oxide formed is adherent thereby giving weight gains rather than weight losses in the sample. The error involved in basing weight losses on uncleaned

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samples decreases as the magnitude of the total loss increases, if amount of adherent oxide is a fairly constant value. However with alloys forming a very adherent corrosion product which increases as the magnitude of total loss increases, error decreases little.

Table II gives data on weight changes during test of alloys 1,5 and 3,4 based on uncleaned samples. This data is shown in Figures II and III for alloys 1,5 and 3,4 respectively, along with data based on cleaned samples of the same alloys. Alloy 1,5 is attacked much more rapidly than alloy 3,4.

TABLE II

CORROSION OF TUBALLOY-MOLYBDENUM ALLOYS IN BOILING WATER AT 100°C
Weight losses expressed in mg/cm² figured from start of test and based on uncleaned samples and on original surface areas.

Days in Test	Alloy Number	
	1,5	3,4
1	0.2	0.02
	0	0.03
2	6.4	-0.02 (gain)
	6.4	-0.08 (gain)
4	18.3(w)	0.7
	19.8(w)	0.2
8	44.5(w)	1.3
	45.2(w)	1.2
16	91.2(w)	3.1
	94.9(w)	-
32	187.3(w)	8.9
	205.9(w)	-

(w) Indicates that the sample was washed with water, wiped, and given an acetone dip.

4.3 Cleaning of Tuballoy-Molybdenum Alloys. Tuballoy-molybdenum alloys 1,4, 1,5, 3,4, and 3,5 were easily cleaned in 25 weight percent nitric acid at 26°C. Figure IV shows typical cleaning curves for these alloys. Samples clean to a pale bronze metallic surface in five minutes or less, thus the 5 minute point gives a maximum value for the corrosion loss of the sample. A minimum value for the corrosion loss is taken as the point of intersection of the ordinate with the best straight line drawn through the level portion of the cleaning curve which represents the rate of solution of clean metal. Weight losses may be reported with an estimated accuracy of 0.1 mg/cm².

Cleaning of the furnace cooled alloys (alloys 2,4 and 2,5) was more difficult, since they were found to be highly reactive in 25 weight percent nitric acid at 26°C. Nitric acid produces a dark grey surface even on

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FIGURE II
COMPARISON OF CORROSION LOSSES OF ALLOY 1,5 BASED ON
CLEANED AND UNCLEANNED SAMPLES

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FIGURE III

COMPARISON OF CORROSION LOSSES OF ALLOY 3,4 BASED ON CLEANED
AND UNCLEANNED SAMPLES

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FIGURE IV

CLEANING OF ALLOYS 3,4 and 3,5 in 25 WEIGHT PERCENT HNO_3
AT ROOM TEMPERATURE

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mechanically cleaned base metal. The following list gives the various cleaning solutions tried:

- (a) 20 weight percent HNO_3 at 26°C .
- (b) 40 weight percent HNO_3 at 30°C .
- (c) 1 part HNO_3 (70 wt.%) to 20 parts glacial acetic (by volume) at 27°C .
- (d) "Concentrated" H_2SO_4 (95%) saturated with $\text{Na}_2\text{Cr}_2\text{O}_7$ at 26°C .

None were very successful possibly because these furnace cooled alloys are subject to intergranular or transgranular attack by the cleaning reagents tried.

Details of the cleaning of the tuballoy-molybdenum alloys are given in the Appendix.

4.4 Results. The tuballoy-molybdenum alloys were not observed to go through any color changes while in test. The corrosion product which forms on them is always a black oxide, but its nature varies. The corrosion product on alloys 1,4 and 1,5 was very loose and nearly all of it fell off in test. The portion left on removal from test tended to crumble off and was largely removed by washing the sample in water and then wiping. The corrosion product on alloys 2,4, 2,5, 3,4, and 3,5 was rather adherent. The corroded surfaces of alloys 2,4 and 2,5 resembled sandpaper in appearance and feel. On alloys 3,4 and 3,5 the corrosion product tended to scale off.

In the case of alloy 1,4 and 1,5 where much corrosion product fell off the sample during test, the product which collected in the bottom of the beaker was observed to be a deep purple color which gradually turned to a bright yellow.

Alloys 2,4 and 2,5 cracked while in test (see Figure I). Four samples, two of alloy 2,4 and two of alloy 2,5, were run in 1, 2, 4, 8, and 16 day tests successively. At the end of the 16 day test, alloy 2,4 contained small cracks and the edges of the samples were very ragged. Alloy 2,5 also contained cracks and a large piece was cracked off one of the samples. Another sample of alloy 2,5 was started for a 32 day run. After 20 days in test, a large piece cracked off. This cracking may account for the lack of a linear weight loss - time relation for these alloys.

Tables III and IV contain corrosion data based on cleaned samples. These data are shown on a comparative basis in Figure V; they are also shown in Figures VI, VII, and VIII.

A list of the approximate slopes of the curves shown in Figure V are given below. They are based on tests which range from 1 to 32 days in length.

Alloy	Approximate Slope (mg/cm ² /hr)
3,4	0.02
3,5	0.03
2,4	0.07)
2,5	0.07) --(initial slopes)
1,4	0.18
1,5	0.26
Std. Tu	2.7

TABLE III

CORROSION OF TUBALLOY-MOLYBDENUM ALLOYS IN BOILING WATER AT 100°C
Weight losses expressed in mg/cm² figured from start of test and
based on original areas)

Days in Test	Alloy Number					
	1,4	2,4	3,4	1,5	2,5	3,5
1	0.6(a) 0.9(a)	1.9(a) 1.5(a)	0.3(a) 0.3(a)	1.3(a) 0.8(a)	0.8(a) 1.7(a)	1.0(a) 1.1(a)
2	5.5(a) 6.6(a)	3.5(a) -	1.2(a) 1.2(a)	7.1(a) 7.1(a)	3.2(d) 2.1(e)	1.5(a) 1.7(a)
4	21.1(a) 20.2(a)	5.0(a) 4.5(a)	2.1(a) 2.1(a)	19.0(a) 20.9(a)	7.2(a) 6.8(a)	3.1(a) 5.0(a)
8	35.6(a) 29.2(a)	12.5(b) 12.5(b)	3.3(a) 3.1(a)	45.5(a) 46.3(a)	12.7(b) 32.5(b)	4.9(a) 5.1(a)
16	77.4(a) 66.8(a)	12.0(b) 11.3(a)	10.7(a) -	92.6(a) 96.4(a)	29. (a) -	13.1(a) -
24	89.1(a) 100.6(a)	- -	- -	- -	- -	- -
32	127.8(a) 143.1(a)	20.8(c) 19.3(c)	18.4(a) -	207.3(a) 189.0(a)	41. (c) -	20.9(a) -

Cleaning methods:

- (a) 25 weight percent HNO₃ at 26°C.
- (b) "Concentrated" H₂SO₄ (95%) saturated with Na₂Cr₂O₇ at 26°C.
- (c) 1 part HNO₃ (70%) to 20 parts glacial acetic acid (by volume) at 27°C.
- (d) 40 weight percent HNO₃ at 3°C.
- (e) 20 weight percent HNO₃ at 26°C.

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TABLE IV

CORROSION OF TUBALLOY-MOLYBDENUM ALLOYS IN BOILING WATER AT 100°C
Weight losses expressed in mg/cm²/hr figured from start of test
and based on original areas)

Days in Test	Alloy Number					
	1,4	2,4	3,4	1,5	2,5	3,5
1	0.022(a) 0.034(a)	0.026(a) 0.068(a)	0.011(a) 0.012(a)	0.054(a) 0.035(a)	0.038(a) 0.078(a)	0.040(a) 0.045(a)
2	0.117(a) 0.140(a)	0.074(a) -	0.025(a) 0.024(a)	0.147(a) 0.147(a)	0.068(d) 0.045(e)	0.032(a) 0.036(a)
4	0.22(a) 0.21(a)	0.051(a) 0.046(a)	0.023(a) 0.022(a)	0.20(a) 0.22(a)	0.074(a) 0.070(a)	0.032(a) 0.052(a)
8	0.18(a) 0.152(a)	0.065(b) 0.065(b)	0.020(a) 0.019(a)	0.246(a) 0.250(a)	0.066(b) 0.169(b)	0.030(a) 0.031(a)
16	0.202(a) 0.174(a)	0.031(b) 0.031(a)	0.028(a) -	0.243(a) 0.253(a)	0.076(a) -	0.034(a) -
24	0.155(a) 0.175(a)	- -	- -	- -	- -	- -
52	0.167(a) 0.187(a)	0.027(c) 0.025(c)	0.024(a) -	0.272(a) 0.248(a)	0.053(c) -	0.028(a) -

Cleaning methods:

- (a) 25 weight percent HNO₃ at 26°C.
- (b) Concentrated H₂SO₄ (95%) saturated with Na₂Cr₂O₇ at 26°C.
- (c) One part HNO₃ (70%) to 20 parts glacial acetic acid (by volume) at 27°C.
- (d) 40 weight percent HNO₃ at 30°C.
- (e) 20 weight percent HNO₃ at 26°C.

4.5 Conclusions. The tuballoy-molybdenum alloys which were melted in BeO crucibles seem to be slightly more corrosion resistant in boiling water than those alloys which were melted in graphite crucibles.

The heat treatment also affects the rate of corrosion in boiling water. As compared with the alloys with a No. 3 heat treatment, those with a No. 1 heat treatment corrode approximately ten times more rapidly; those with a No. 2 heat treatment corrode approximately twice as rapidly, but crack after about 16 days in test.

Standard tuballoy corrodes in distilled water at 100°C approximately 135 times as fast as the best tuballoy-molybdenum alloy (alloy 3,4) and about 10 times as fast as the least corrosion resistant alloy (alloy 1,5).

FIGURE V

CORROSION DATA ON 5 WEIGHT PERCENT MOLYBDENUM ALLOYS
(Tested in Boiling Distilled H₂O at 100°C)

FIGURE VI

CORROSION OF ALLOYS 1,4 and 1,5 IN BOILING WATER AT 100°C (based on samples cleaned in 25 weight percent HNO_3 at 26°C).

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FIGURE VII

(based on samples cleaned as in Table III)

FIGURE VIII

CORROSION OF ALLOYS 3,4 and 3,5 IN BOILING WATER AT 100°C
(based on samples cleaned in 25 weight percent HNO₃ at 26°C)

5. EFFECT OF VARYING THE PERCENT OF MOLYBDENUM IN AS-CAST TUBALLOY-MOLYBDENUM ALLOYS

Before the hot rolled tuballoy-molybdenum alloys were tested, preliminary testing was done on a series of as-cast tuballoy-molybdenum alloys of varied composition. These alloys were tested in boiling distilled water at 100°C. The purpose was to determine the relation between corrosion resistance and the molybdenum content of the alloys.

The tests were carried out in the manner described in the first paragraph of 4.1.

The samples were given a standard preparation before being placed in test. They were finished by hand polishing on No. 2 grit emery paper, and the surface areas were measured. They were then dipped in 25 weight percent nitric acid at 28°C for 5 minutes, washed in water, dipped in acetone, weighed, and started in test.

The tests which were run were of short duration, varying in length from 6 to 18 hours. At the end of each test the sample was cleaned by a 5 minute dip in 25 weight percent nitric acid at 28°C.

The results of these tests are given in Table V and are shown graphically in Figure IX.

TABLE V
CORROSION OF AS-CAST TUBALLOY-MOLYBDENUM ALLOYS OF VARYING COMPOSITION IN
BOILING WATER AT 100°C
(Weight losses based on cleaned samples and original surface areas)

Alloy No.	Wt. % Mo.	Weight Loss		Time (hr)	Average weight loss from start of test (mg/cm ² /hr)
		(mg)	(mg/cm ²)		
Std. Tu	None	-	-	-	2.7
X133 A	0.15	356.5	20.3	6.0	3.38
X133 B	0.15	925.1	52.0	11.0	4.71
X133 C	0.15	926.4	54.5	11.0	4.95
X134 A	0.30	881.1	44.9	11.7	3.83
X134 B	0.30	457.3	24.3	11.7	2.08
X130 A	0.61	472.3	30.9	17.7	1.74
X130 B	0.61	401.4	31.9	17.7	1.80
X135 A	1.53	189.3	15.6	15.2	1.03
X135 B	1.53	202.6	15.0	15.2	0.998
X131 A	3.09	259.6	17.2	17.2	1.00
X131 B	3.09	263.1	16.2	17.2	0.938
X136 A	6.31	14.3	1.5	6.0	0.246
X136 B	6.31	2.4	0.3	6.0	0.045

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FIGURE IX

CORROSION OF "AS-CAST" TUBALOY-MOLYBDENUM ALLOYS IN BOILING DISTILLED WATER (100°C)

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It appears that small amounts of molybdenum (up to 0.25 weight percent) increase the rate of corrosion, since standard tuballoy corrodes at an average rate of $2.7 \text{ mg/cm}^2/\text{hr}$; however, increasing amounts of molybdenum (from 0.25 to 6 weight percent) decrease the corrosion rate.

Comparison of the data of Tables IV and V clearly indicates that the corrosion resistance of the fabricated and properly heat treated alloys is superior to that of alloys of the same composition in the "as cast" condition.

Preliminary autoclave test of "as cast" alloy containing 6.3 weight percent molybdenum showed that this material was attacked internally (CT 3043). In order to determine whether similar attack occurs at 100°C , a sample was exposed in boiling distilled water for 18 days. Figure X shows some of the cracked fragments of the sample after this exposure.

6. APPENDIX

6.1 Development of Cleaning Procedures for Tuballoy-Molybdenum Alloys.

(a) Cleaning of Water Quenched Tuballoy-Molybdenum Alloys.

A method for removing corrosion product from water corroded tuballoy-molybdenum alloys without removing appreciable amounts of the underlying metal was desired. Corrosion rates are determined from "cleaned weights" of corroded samples (i.e., the weight of the unaltered metal from which the corrosion product has been removed). The accuracy of the cleaning method limits the accuracy of the corrosion rate. Since 25 weight percent nitric acid at 26°C was found suitable for cleaning corroded tuballoy, nitric acid solutions were also tried on the tuballoy-molybdenum alloys.

The alloys of tuballoy-molybdenum which are water quenched from 850°C or tempered at 350°C for 24 hours after water quenching were found to clean easily in 25 weight percent nitric acid at 26°C , as does standard tuballoy. Typical cleaning curves on these alloys are shown in Figure XI. Samples clean to a pale bronze metallic surface in 5 minutes or less, thus the 5 minute point gives a maximum value for the corrosion loss of the sample. A minimum value for the corrosion loss is taken as the point of intersection of the ordinate with the best straight line drawn through the level portion of the cleaning curve which represents the rate of solution of the clean metal.

In most cases the difference in the maximum and minimum values of the corrosion loss determined this way was negligible, and the value as determined by a 5 minute dip in 25 weight percent nitric acid at 26°C was reported. Weight losses in alloys 1,4 , 1,5 , 3,4 , and 3,5 due to water corrosion can be reported with an estimated accuracy of 0.1 mg/cm^2 .

(b) Cleaning of Furnace Cooled Tuballoy-Molybdenum Alloys. The furnace cooled alloys 2,4 and 2,5 presented a more difficult cleaning problem in that they were found to be highly reactive in 25 weight percent nitric acid at 26°C . The furnace cooled alloys assume a dark gray metallic surface in dilute or 70% nitric acid. This is probably because the metal is attacked intergranularly. Determination of the point where all corrosion

FIGURE X

DISINTEGRATED "AS CAST" 6.3 WEIGHT PERCENT MOLYBDENUM
ALLOY AFTER 18 DAYS IN BOILING DISTILLED WATER (100°C)

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FIGURE XI

CLEANING OF ALLOYS 1,5 and 1,4 IN 25 WEIGHT PERCENT NITRIC
ACID AT ROOM TEMPERATURE

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product had been removed was difficult. Lowering the weight percent of nitric acid to 10 and 20 percent did not prevent attack of the metal to any appreciable degree and similar cleaning curves were obtained. Figures XII-A, XII-B, XII-C show the type of cleaning curves obtained in cleaning the furnace cooled alloys in 20 and 25 weight percent nitric acid at room temperature (about 26 to 28°C). The weight losses determined by these methods are estimated to be accurate within 0.5 mg/cm² when the total amount of corrosion loss is about 2.5 mg/cm² and within 1.0 to 1.5 mg/cm² when the total amount of corrosion loss is larger than 5.0 mg/cm².

It was desirable to find an agent which could be used to clean these furnace cooled alloys with better accuracy, consequently several other methods were tried. A 40 weight percent nitric acid solution at 3°C and a solution of 20 parts glacial acetic acid to 1 part (70%) nitric acid (by volume) at 27°C were tried and showed no improvement over the previous methods tried.

"Concentrated" sulphuric acid (95%) saturated with sodium dichromate at 26°C showed a cleaning curve of the type shown in Figure XII-D. The large weight loss during the first ten minutes in the solution is due mainly to loosening of the corrosion product by the cleaning solution. The rate of metal attack in this solution is slow; however, blackening of metallic samples does occur due probably to intergranular attack of the metal.

In this method, a maximum value for the corrosion loss is taken at the point where the sample appears gray-metallic; a minimum is taken as the intersection of the ordinate with the best straight line drawn through the level portion of the curve which represents the rate of solution of clean metal. The accuracy of weight losses determined by this method is estimated to be about 0.5 mg/cm².

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FIGURE XII-A

CLEANING OF 2,5 ALLOY IN 20 WEIGHT PERCENT HNO_3
 26°C

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FIGURE XII-B

CLEANING OF 2,5 ALLOY IN 25 WEIGHT PERCENT HNO_3 at 26°C

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FIGURE XII-C

CLEANING OF ALLOY 2,4 in 25 WEIGHT PERCENT HNO_3 at 26°C

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FIGURE XII-D

CLEANING ALLOY 2,4 IN "CONCENTRATED" H_2SO_4 SATURATED WITH $\text{Na}_2\text{Cr}_2\text{O}_7$ at 26°C .

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6.3 Secret Notebook References:

Autoclave data:- Notebook 1175B, pp.10,17,28,29,30,31.
Notebook 359C, pp. 3,5,21,33,36,37.

Boiling Water Test Data:-

- (a) 5% Molybdenum Alloys - Notebook 354C.
- (b) As-cast Tuballoy-Molybdenum Alloys of varying composition - Notebook 461, pp.187-189.

Cleaning Data:- Notebook 353C, and 354C.

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