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FINAL REPORT ON THE RESULTS OF
EXPOSURE OF TUBALLOY AT ELEVATED
TEMPERATURE IN AIR, NITROGEN, AND
NEUTRAL ATMOSPHERES

By

W. E. Lindlief and V. C. F. Holm

February 10, 1945

National Bureau of Standards
Washington, D. C.

UNITED STATES ATOMIC ENERGY COMMISSION
Technical Information Service, Oak Ridge, Tennessee

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Errata for CT-M-2733

Since the figures for report CT-M-2733 were assembled incorrectly when the report was issued, please use the following list for proper location.

Section A - Oxidation of tuballoy in air at temperature up to 500°C.

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Fig. 1. Furnace Assembly for the Study of the Scaling of Tuballoy in Air.	page 2	page 1
Fig. 2. Behavior of M and I Metals when Exposed to Air at Indicated Temperatures.	page 4	page 4
Fig. 3. Behavior of M and I Metals when Exposed One Hour to Air at Indicated Temperatures.	page 4 and Fig. 2	p. 4 and Fig. 2
Fig. 4. Behavior of M and I Metals when Exposed to Air at Indicated Temperatures.	page 5	page 5
Fig. 5. Behavior of Sheet and Block Specimens of I Metal of Some Surface Area when Exposed to Air at 400°C.	p. 5 and Fig. 4	p. 5 and Fig. 4
Fig. 6. Appearance of M & I Metals After Exposure for 1 Hour to Air at Temperatures Indicated and Appearance of Scale Formed.	p. 5 and Figs. 4-5	p. 5 and Figs. 4-5
Fig. 7. Relation Between Gain in Weight per Unit Area and Penetration of Metal on Oxidizing Tuballoy.	p. 6	p. 5 and Figs. 4-5-6

Section B - Action of Nitrogen on Tuballoy at temperatures up to 850°C.

	At present following	Should follow
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DATE FEB 20 1957 *Ofs*

For The Atomic Energy Commission

H. F. Canell

Chief, Declassification Branch

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Report of February 10, 1945

from

Metallurgical Laboratory

[National Bureau of Standards]

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W. E. Lindlief

B ----- Action of Nitrogen on Tuballoy at Temperatures up to 850°C
W. E. Lindlief

C ----- Bright Annealing of Tuballoy
V. C. F. Holm and W. E. Lindlief.

Report Received: March 19, 1945

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THE OXIDATION OF TUBALLOY IN AIR AT TEMPERATURES UP TO 500°C.

The action of air on Tuballoy at temperatures up to 500°C was studied by measuring the gain in weight obtained on exposing samples of the metal to a moving air stream for varying periods of time. The compositions of the oxides formed at various temperatures are not accurately known, but curves for conversion of gain in weight to penetration are included for end products of Tu_3O_8 and TuO_2 , and estimates of penetration corresponding to gain in weight have been obtained from these.

Material and Preparation - Four lots of metal from two sources were used in the experiments, representing the compositions of metal available at the time the tests were started. The analyses of the different lots given below are the averages of top and bottom sections of the 2 1/2 inch diameter ingots from which the scaling samples were fabricated. The two I metals were similar in composition and contained more carbon and silicon than the M metals. The latter were similar in composition except that M-1 contained approximately three times as much iron as M-2, and both contained more iron than the I metals.

Mark Material		Element - percent					
		C	O ₂	N ₂	H ₂	Fe	Si
M-1	M ingot H74	0.023	0.003	0.006	0.0008	0.062	< 0.001
M-2	M ingot H77	.020	.003	.007	.0010	.021	< .001
I-1	A ingot C733	.057	.002	.005	.0009	.005	.014
I-2	A ingot D733	.055	.002	.005	.0012	.006	.013

The scaling samples were about 1 x 3/4 inch and 0.06 to 0.08 inch thick (surface area about 10 sq cm.) and were fabricated from 1/2 inch thick discs cut from the ingots. The M-1, M-2, and I-2 samples were hot rolled from this thickness to about 0.08 inch, starting at a temperature of 600°C and without intermediate reheating. They were finally given several straightening passes cold, the reduction by cold-rolling being about 10 percent. The I-1 samples, prepared by forging and cold-rolling, were hot forged at 600°C from 1/2 inch to 0.34 inch thickness, then cold rolled with frequent anneals to about 0.06 inch thickness. The reduction by cold-rolling after the final anneal was about 26 percent.

Method - Attempts were first made to study oxidation quantitatively by measuring the decrease in weight on pickling scaled samples, but no pickling solution was developed which removed the scale without attacking the base metal to a degree which made the loss in weight data uncertain. Anodic removal of the scale in various electrolytes was also investigated, but some solution of the base metal always resulted. Shot blasting to remove scale eroded the base metal severely and the method finally adopted involved the measurement of gain in weight produced by oxidation.

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The furnace assembly used for the scaling experiments is shown in figure 1. The samples were held in number 00 porcelain crucibles, the function of which was to catch any oxide which flaked off. The diameter of the crucibles at the bottom was less than the specimen width, consequently the samples did not rest on the bottom of the crucibles but were supported by the side walls, allowing for air circulation around the specimens. Four crucibles were held in a stainless steel

FIG. 1 - ASSEMBLY FOR BRIGHT ANNEALING TUBALLOY IN PURIFIED HELIUM.

A - ANHYDRONE (MAGNESIUM PERCHLORATE)
 B - MERCURY SEAL
 C - TWO WAY STOPCOCK
 D - ACTIVATED CHARCOAL
 E - LIQUID AIR

F - FLEXIBLE COPPER TUBING
 G - STOPCOCK
 H - VYCOR TUBE
 I - SAMPLE CONTAINER
 J - FURNACE (OPERATING POSITION)

K - FURNACE THERMOCOUPLE
 L - FURNACE (PREHEATING POSITION)
 M - SPECIMEN THERMOCOUPLE
 N - MERCURY MANOMETER
 O - BUBBLER

0 3 6 9 12
 SCALE - INCHES

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FIG. 1 - SAMPLE CONTAINER USED IN NITROGEN SCALING TESTS.

0 1 2
SCALE - INCHES

FIG. 2 - ASSEMBLY FOR THE STUDY OF THE SCALING OF TUBALLOY IN PURIFIED NITROGEN AT ELEVATED TEMPERATURES.

A - ANHYDRONE (MAGNESIUM PERCHLORATE)	G - FLEXIBLE COPPER TUBING	M - FURNACE (PREHEATING POSITION)
B - COPPER WIRE AT APPROXIMATELY 550° C	H - STOPCOCK	N - SPECIMEN THERMOCOUPLE
C - MERCURY SEAL	I - VYCOR TUBE	O - MERCURY MANOMETER
D - TWO WAY STOPCOCK	J - SAMPLE BOAT	P - TWO WAY STOPCOCK
E - ASCARITE	K - FURNACE (OPERATING POSITION)	Q - BUBBLER
F - PHOSPHORUS PENTOXIDE	L - FURNACE THERMOCOUPLE	

0 3 6 9 12
SCALE - INCHES

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FIG. 2 - APPEARANCE OF TUBALLOY SPECIMENS ANNEALED IN PURIFIED
— HELIUM OR IN VACUUM AT INDICATED TEMPERATURES. —

- X 1 -

FIG. 3 - APPEARANCE OF ORIGINAL AND BRIGHT ANNEALED TUBALLOY -
SPECIMENS BEFORE AND AFTER EXPOSURE TO LABORATORY ATMOSPHERE.

- X 1 -

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disc, the diameter of which was about 1/2 inch less than that of the silica furnace tube and holes in the disc allowed free circulation of air. The thermocouple for furnace temperature measurements was in a steel tube at the center of the furnace, and was calibrated to indicate the temperature of the specimen containers within $\pm 5^{\circ}\text{C}$. Actual specimen temperatures were also taken for many runs with a second couple wedged into a slit in the specimen. Air circulation was maintained by a laboratory vacuum line attached to the bottom of the furnace. The standard rate of flow, measured with a gas meter, was about 2 liters of air per minute. Tests showed that wide variations in the rate of air flow did not affect scaling rates.

Samples were cleaned on 1-G abrasive paper, washed in alcohol and ether, dried in a vacuum desiccator and weighed just prior to insertion in the preheated furnace. After oxidation the samples were cooled in a desiccator and reweighed. The times of oxidation referred to throughout the report are the times the specimens were in the hot furnace and not actual times at temperature. At temperatures up to and including 300°C , the time involved in heating specimens to furnace temperature was 10 to 15 minutes; above 300°C the specimens reached furnace temperature more quickly (in 3 to 5 minutes) due to the heat liberated by their rapid oxidation. Exposures of less than 1/2 hour were not recorded for temperatures below 350°C , because of the relatively long heating period involved and because of the slight action of air on Tuballoy at these temperatures.

Experimental Results - Preliminary experiments showed that better reproducibility of results was obtained at moderate temperatures than at either high or low temperatures. At low temperatures, e.g., 100°C , the gain in weight of the specimen was less than 1 milligram and, consequently, errors in weighing made the numerical results uncertain. At temperatures above 300°C , oxidation was rapid and the oxide scale was irregularly non-adherent but at temperatures of about 200°C the scale was adherent and the rate of oxidation was enough to create reliably determinable increases in weight. The reproducibility of results at about 200°C was demonstrated by two experiments. In the first run four specimens of I metal were exposed simultaneously at 195°C . The resulting gains in weight ranged from 1.2 to 1.8 mg per cm^2 , or covered a range of $\pm 20\%$ from a mean value of 1.5 mg per cm^2 . In the other run, four similar specimens exposed at 205°C varied from 2.3 to 2.8 mg per cm^2 , or covered a range of $\pm 11\%$ from a mean value of 2.6 mg per cm^2 . These results show that individual values are as good as the general run of corrosion tests but they emphasize the necessity for precise control of conditions; and increase in temperature from 195 to 205°C practically doubled the rate of oxidation.

Table I summarizes the oxidation data from individual runs with the results shown graphically in figures 2 and 3. The relationship between time of exposure and oxidation as measured by gain in weight for various temperatures is plotted in figure 2. At 100°C the rate of oxidation was so low that after four hours at this temperature no detectable weight increase occurred, although the specimens were tarnished a deep blue color, and after 20 hours exposure the gain in weight was about $0.1 \text{ mg}/\text{cm}^2$. At 150°C the rate of oxidation was somewhat higher and M and I samples, within the limits of experimental error, were oxidizing at approximately equal rates.

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FIG. 1 - FURNACE ASSEMBLY FOR THE STUDY OF THE SCALING OF TUBALLOY IN AIR.

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At 200°C or higher temperatures the difference in oxidation rate between the two metals becomes apparent, the I metals always oxidizing at a faster rate. At this point the rate varied greatly with small temperature changes, hence the scatter of the plotted points for this temperature, especially for the 1 hour exposures where a temperature increase of 10°C almost doubled the oxidation rate. The scale formed at 200°C was quite adherent and exerted somewhat of a protective action, as evidenced by the change in slope of the curve beyond the two hour period. At 300°C the scale was not as adherent as that formed at the lower temperatures and flaked off when a sufficient thickness was built up. Thus the protective action was not observed and the rate of oxidation did not drop with time of exposure. The oxidation of the I metals was sufficiently rapid when exposed to a furnace temperature of 300°C to raise their temperature slightly above that of the furnace. The temperature of the M metals, oxidizing at the slower rate, remained that of the furnace. A more complete discussion of specimen temperatures and their relation to furnace temperatures is given in subsequent paragraphs.

The rate of oxidation is plotted against furnace temperature for the 1 hour exposures in figure 3. Clearly shown here is the rapid increase in rate of oxidation which occurred at furnace temperatures above 300°C. For both metals oxidation proceeded at a rate which raised specimen temperatures far above those of the furnace. Despite this rapid oxidation rate, check samples on successive runs oxidized at a rate, which, although variable, was consistently of the same order of magnitude.

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FIG. 4 - BEHAVIOR OF M-2 AND RU-557 METALS WHEN EXPOSED TO NITROGEN AT INDICATED TEMPERATURES.

FIG. 5 - RELATION BETWEEN GAIN IN WEIGHT PER UNIT AREA AND PENETRATION OF METAL ON EXPOSURE OF TUBALLOY TO NITROGEN.

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Table I

Data from Oxidation Experiments

Temp. °C	Time in Furnace Hrs.	Gain in Wt., mg/cm ²				Gain in Wt., mg/cm ² /hr			
		M-1	M-2	I-1	I-2	M-1	M-2	I-1	I-2
105	1	0.00	0.00	0.00	0.00	0.000	0.000	0.000	0.000
100	4	.00	.00	.00	.00	.000	.000	.000	.000
105	20	.14	.15	.08	.08	.007	.007	.004	.004
150	1	0.01	0.01	0.01	0.04	0.010	0.010	0.010	0.040
155	2	.3	.4	.3	.3	.15	.20	.15	.15
155	4	.7	.6	.4	.4	.18	.15	.10	.10
205	1/2	0.5, 0.6	0.4	0.6	0.8	1.0, 1.2	0.8	1.2	1.6
205	1	1.0, 1.2	.9	1.3	1.5	1.0, 1.2	.9	1.3	1.5
205	1	1.6	1.9	2.9	2.9	1.6	1.9	2.9	2.9
205	1	1.3	1.5	2.4	2.1	1.3	1.5	2.4	2.1
205	2	2.4, 2.4	2.8	4.9	4.5	1.2, 1.2	1.4	2.4	2.2
200	4	3.1, 3.0	3.1	7.9	5.6	0.8, 0.8	0.8	2.0	1.4
300	1/2	2.5	2.5	2.3	2.5	5.0	5.0	4.6	5.0
305	1	3.7	3.4	5.6	5.8	3.7	3.4	5.6	5.8
305	1	4.3	4.5	6.2	5.1	4.3	4.5	6.2	5.1
310	1	4.2	4.0	5.9	6.3	4.	4.0	5.9	6.3
305	2	5.2	6.3	8.5	7.9	2.6	3.2	4.2	4.0
305	4	9.2	14.7	30.6	—	2.3	3.7	7.7	—
360	1/4	11.6	7.1	14.0	20.5	46.4	28.4	56.0	82.0
355	1/2	23.5	11.4	33.5	33.5	47.0	22.8	67.0	67.0
360	1	46.4	30.4	99.8	94.1	46.4	30.4	99.8	94.1
360	1	38.4	29.2	75.9	68.5	38.4	29.2	75.9	68.5
405	1/4	9.9	7.7	17.2	20.7	39.6	30.8	68.8	82.8
400	1/2	16.5	11.3	31.9	45.2	33.0	22.6	63.8	90.4
400	1	46.3	39.5	108.4	118.8	46.3	39.5	108.4	118.8
405	1	39.2	25.0	103.5	92.3	39.2	25.0	103.5	92.3
405	1	46.5	24.7	87.9	114.5	46.5	24.7	87.9	114.5
500	1/4	12.8	12.7	21.2	25.0	51.2	50.8	84.8	100.0
500	1/2	24.2	22.1	47.6	58.0	48.4	44.2	95.2	116.0

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FIG. 2 - BEHAVIOR OF M AND I METALS WHEN EXPOSED TO AIR AT INDICATED TEMPERATURES.

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FIG. 3 - BEHAVIOR OF M AND I METALS WHEN EXPOSED ONE HOUR TO AIR AT INDICATED TEMPERATURES.

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FIG. 4 - ASSEMBLY FOR THE PURIFICATION OF ARGON.

A - ANHYDRONE (MAGNESIUM PERCHLORATE)	F - PHOSPHORUS PENTOXIDE
B - COPPER WIRE AT 550° C	G - TUBALLOY TURNINGS AT 800° C
C - MERCURY SEAL	H - FLEXIBLE COPPER TUBING
D - TWO WAY STOPCOCK	I - STOPCOCK
E - ASCARITE	J - SAMPLE FURNACE

0 3 6 9 12
SCALE - INCHES

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Figure 4 shows temperatures developed in specimens of both metals exposed at various furnace temperatures. At furnace temperatures of 300°C or lower, the temperatures of the M samples always remained that of the furnace. An I sample at 300°C oxidized at a rate which brought its temperature 10 to 15°C above that of the furnace. At 350 and 400°C, the temperatures of both M and I samples were from 100 to 200°C above those of the furnace. The temperatures fluctuated as the scale formed and then flaked off, dropping as the protective coating built up, which decreased the oxidation rate, and increasing as this oxide dropped off to expose bare metal. The maximum temperature attained by the M-1 metal for a furnace temperature of 400°C was approximately 500°C, while the I sample for the same furnace temperature reached a maximum of 600°C, in line with its higher oxidation rate. These specimen temperature curves are very irregular and not reproducible as they are entirely dependent on the manner in which the scale flakes off.

The temperature of a block specimen of I-2 metal was measured for a furnace temperature of 400°C over a one hour exposure period. Its surface area was roughly equivalent to that of the standard sheet specimens but its mass was about three times as great. The temperatures of both types of specimen are plotted in Figure 5. The block specimen reached temperature more slowly than the sheet specimen but ultimately attained a temperature above that of the thinner sample. It is evident that changes in mass of this order have little effect on the surface temperature of the specimen, i.e., heavier specimens oxidize at about the same rate as thin slabs or sheet.

The appearance of Tuballoy samples after exposure for one hour to air at various temperatures is shown in Figure 6. At 200°C the scale was adherent and practically none flaked off during oxidation periods up to four hours. At 300°C a small amount flaked off after the 1 hour run as shown in the photograph and with longer oxidation periods at this temperature correspondingly more dropped off. Above 300°C, the scale formed in sheets or laminae of varying thicknesses and dropped off as such. The laminae formed at 350°C were thin and fragile and broke down readily into a powder. At 400°C thick laminae of oxide, which dropped off without breaking, were formed particularly on the I metals. Some of these laminae were as much as 0.075 inch in thickness.

Composition of Scale - The gain in weight figures may be converted to depth of penetration of base metal if the composition of the scale formed is known. Obviously the scale consists principally of oxides, and it is unlikely that nitrides are formed at any temperature in the presence of an excess of oxygen, and it is known that nitride is readily converted to oxide in air at low temperatures. The nitrogen content of the M and I scale produced at 400°C was determined by chemical analysis as 0.001 percent. According to available information Tu_3O_8 is the only oxide formed at 400°C or higher temperatures, below this temperature TuO_3 and TuO_2 are reported to form in varying proportions. The curves of figure 7 are included for conversion of gain in weight per unit area to approximate inches penetration, for end products of TuO_3 or Tu_3O_8 . For scaling temperatures at or above 400°C, the Tu_3O_8 curve should be used, at lower temperatures the conversion factor lies between the TuO_3 and Tu_3O_8 curves. The curves are based on a density of 18.9 for Tuballoy.

Combining the data of Table I with the curves of figure 7 shows that the initial rate of attack at 200°C is only a small fraction of one-thousandth of an inch penetration per hour, and the rate decreases as the adherent film increase in

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FIG. 4 - BEHAVIOR OF M AND I METALS WHEN EXPOSED TO AIR AT INDICATED TEMPERATURES.

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FIG. 5 - BEHAVIOR OF SHEET AND BLOCK SPECIMENS OF I METAL OF SAME SURFACE AREA WHEN EXPOSED TO AIR AT 400 °C.

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200° C

300° C

350° C

400° C

I-2 METAL

200° C

300° C

350° C

400° C

M-1 METAL

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FIG.-6 - APPEARANCE OF M AND I METALS AFTER EXPOSURE FOR 1 HOUR TO
—AIR AT TEMPERATURES INDICATED AND APPEARANCE OF SCALE FORMED.—

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in thickness. At 300°C the film is not completely adherent and the progressive oxidation is equivalent to destruction of about 0.001 inch per hour of I metal and about 1/3 or 1/4 of 0.001 inch per hour of M metal. At temperatures between 350 and 500°C, the rate of attack is equivalent to about 0.004 inch penetration per hour for M metal and about 0.01 inch per hour for I metal.

To determine if a nitride scale would protect Tuballoy from oxidation in air, a sample was given a light nitride scale by heating for four hours at 500°C in purified nitrogen. This sample, together with an uncoated sample, was then exposed to air at 300°C for four hours. The oxygen pickup by the bare sample was 7.5 as compared to 1.8 mg/cm² for the nitride coated sample. The nitride scale apparently afforded some protection against oxidation at 300°C. In other experiments it was found that Tuballoy nitride ignited in air at temperatures of 400°C or higher was converted to oxide almost instantaneously; at lower temperatures the conversion proceeded more slowly. The nitride scale would therefore be expected to be effective as a protection against oxidation only at temperatures of 300°C or lower, and even here the action would be only a delaying one rather than one of complete protection.

Summary and Conclusions - Studies of the rate of oxidation of samples of Tuballoy from two sources at temperatures between 100 and 500°C lead to the following conclusions:

- (1) The coating formed in air at any temperature apparently consisted only of Tuballoy oxides.
- (2) The oxide coating formed at 200°C or lower temperatures was adherent and apparently exerted a protective action when a sufficient thickness was attained. At 300°C or higher temperatures the scale formed was not adherent and consequently did not protect the underlying metal.
- (3) A significant difference in oxidation rate at 200°C or higher temperatures was found for metal from two sources, that of I metal being higher than that of M metal. The analytical data show that the I metals contained more carbon and silicon but less iron than the M metals; iron may have a stimulating effect on the rate of oxidation for M-1 contained about three times as much iron as M-2, and its oxidation rate at or above 300°C was substantially higher than that of M-2.
- (4) Exposure of Tuballoy to air at temperatures of 100°C, or less, produced a tarnish film. At 200°C a film less than 0.0005 inch thick is produced in 2 hours and the subsequent rate of attack is lowered because of the presence of this film. At 300°C the rate of penetration is less than 0.0005 inch per hour but there is no protective action. At temperatures between 350° and 500°C, the rate of attack is constant with increasing time, at about 0.004 inch penetration per hour for M metal and 0.01 inch per hour for I metal.
- (5) Tuballoy must be protected if it is to be exposed to air at temperatures above 300°C but protection is not needed for exposure to air at 200°C or less, for reasonable lengths of time.

FIG. 7 - RELATION BETWEEN GAIN IN WEIGHT PER UNIT AREA AND PENETRATION OF METAL ON OXIDIZING TUBALLOY.

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THE ACTION OF NITROGEN ON TUBALLOY AT TEMPERATURES UP TO 850°C.

The action of nitrogen on Tuballoy at elevated temperatures and atmospheric pressure was studied by measuring the gain in weight resulting from exposure of samples of the metal to a stream of purified nitrogen for varying periods of time at temperatures from 300 to 850°C. The data are reported as gain in weight per unit area and a curve is included for conversion of these figures to penetration of base metal.

Material and Preparation - Specimens from five lots of metal were used for some or all of the scaling tests, depending upon the amount of metal available for each lot. Compositions of the various materials are given in the following table. The main differences in composition were the lower carbon and higher iron content of the M metals, and the relatively higher silicon content of the I metals.

Mark	Material	Element - percent					
		C	O ₂	N ₂	H ₂	Fe	Si
M-1	M ingot H 74	0.023	0.003	0.006	0.0008	0.062	0.001
M-2	M ingot H77	.020	.003	.007	.0010	.021	.001
I-1	A ingot C733	.057	.002	.005	.0009	.005	.014
I-2	A ingot D733	.055	.002	.005	.0012	.006	.013
RU-557	Extruded rod	.050	.004	.001	---	.005	---

The samples used for the exposure tests were approximately $3/4 \times 1/2 \times 0.06$ inch, with total surface area of about 5 sq cm. each. The M and I samples were cut from sheet metal prepared by hot and cold rolling as described in detail for the samples used in the oxidation tests. The samples of RU-557 metal were cross sections of the extruded rod, cut to the desired thickness with an abrasive cutoff wheel. Immediately before the exposure test, each sample was cleaned on 1-G abrasive paper, washed in alcohol and ether, and dried in a vacuum desiccator.

Method - As with the oxidation experiments the method adopted for determining scaling rate involved the measurement of gain in weight of samples of Tuballoy when exposed to nitrogen for various times at several temperatures. Because the scale formed at some temperatures popped off violently when the samples cooled and would be lost through scattering, it was necessary to use a covered container for the samples in the exposure tests. The container shown in figure 1 was made from two aluminum boats and contained three compartments with porcelain spacers fitted into grooves in the top and bottom. Three samples could be run simultaneously, for the perforations in the spacer plates were small enough to prevent inter-mixing of the scale in the several compartments.

Preliminary experiments showed that the tank nitrogen should be purified for these experiments. Samples of Tuballoy exposed to unpurified nitrogen gained appreciably in weight during a four hour exposure at 300°C and were completely converted to powder in four hours at 800°C. These results, and analysis of the powder produced at 800°C, showed that the tank nitrogen contained objectionable amounts of oxygen. A purification train was installed, to remove oxygen and water vapor from the nitrogen. Samples of Tuballoy exposed in the purified gas for four hours at 300°C gained less than 0.1 mg/cm², which is less than one twentieth of the gain in weight in unpurified gas. This indicates that the purification method was satisfactory.

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A new furnace was used for the nitrogen experiments because the furnace used for the oxidation runs could not be satisfactorily swept out and maintained free from oxygen.

The assembly for nitrogen purification and the furnace in which the samples were exposed to the purified nitrogen are shown in figure 2. The purification train consisted of a drying tube containing Anhydron (anhydrous magnesium perchlorate), a hot copper furnace for oxygen removal, a tube containing the CO₂ absorbent Ascarite, and final drying tubes containing Anhydron and phosphorus pentoxide respectively. After the samples were placed in position, the Vycor furnace tube was alternately evacuated and flushed with nitrogen from purification train. While this was in progress the furnace was brought to the desired temperature at position M. When the furnace was at temperature and the tube was thoroughly flushed, the run was started by sliding the hot furnace to position K, over the specimens. Separate thermocouples were used to indicate temperatures of the furnace and specimens. Between runs the stopcock at the exit end of the purification train was kept closed to prevent contamination. A slow rate of flow of nitrogen, not exceeding 2 liters per hour, was maintained during the runs.

Results of the exposure tests in purified nitrogen are given in Table I.

Table I

Data from Exposures in Purified Nitrogen

Temp. °C	Time Hrs.	Gain in Wt., mg/cm ²					Gain in Wt., mg/cm ² /hr				
		M-1	M-2	I-1	I-2	RU557	M-1	M-2	I-1	I-2	RU557
300	4	<0.01	<0.01	<0.01	<0.02	---	<0.003	<0.003	<0.003	0.005	---
400	4	.04	.01	.02	---	0.02	.010	.003	.005	---	0.005
500	4	---	.5	---	.4	.4	---	.12	---	.10	.10
500	4	---	.5	---	---	.5	---	.12	---	---	.12
600	4	2.0	1.9	1.5	---	1.2	.50	.48	.39	---	.30
700	4	---	4.3	---	---	4.6	---	1.1	---	---	1.2
760	4	---	4.5	---	---	4.4	---	1.1	---	---	1.1
800	4	---	*	72.7	---	*	---	*	18.2	---	*
850	4	---	*	---	---	*	---	*	---	---	*
700	1	---	1.8	1.3	---	1.5	---	1.8	1.2	---	1.5
700	2	3.1	3.9	---	---	2.0	1.6	2.0	---	---	1.0
700	2	---	---	---	3.1	2.7	---	---	---	1.6	1.4
700	4	---	4.3	---	---	4.6	---	1.1	---	---	1.2
700	16	---	8.4	---	---	8.7	---	.53	---	---	.54
700	30	---	10.9	12.2	---	5.6?	---	.36	.41	---	.19?
800	1	---	20.9	---	---	29.5	---	20.9	---	---	29.5
800	2	---	64.4	---	---	96.0	---	32.2	---	---	48.0
800	4	*	*	72.7	---	*	*	*	18.2	---	*

* - Completely converted to nitride.

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In contrast to the oxidation experiments, there is little or no effect of composition of the metal. Samples of all the metals behaved so much alike in nitrogen at all temperatures that figure 3, which was plotted for M-2 and RU-557 samples, is equally representative of M-1, I-1, and I-2. At 300 and 400°C, the reaction proceeded slowly and the gain in weight after four hours at these temperatures was almost negligible. At 500 and 600°C the reaction proceeded more rapidly; an appreciable gain in weight occurred with a four hour exposure and the samples became covered with a tenacious black scale which had a decided metallic luster. At 700 and 750°C increasingly more of the black scale was formed which was apparently adherent until the samples were cooled, when parts of it (in small pieces and only a fraction of the total) popped off violently. This popping off of scale often continued for some time after the samples were cooled to room temperature. The scale that did remain on the samples was very adherent and could not be scraped off nor could it be cracked off by gentle hammering. At 800°C and higher temperatures nitrogen attacked Tuballoy so rapidly that in four hours or less the samples of about 0.06 inch thickness were completely converted to a dull gray powder, non-metallic in appearance.

Figure 4 illustrates the great difference in the rate of attack of nitrogen at 700°C (or 750°C) and at 800°C. This difference presumably is associated with the beta-gamma transformation in the metal. At 700°C there was initial attack at a moderate rate but after a few hours the rate dropped appreciably, because of the protective action of the adherent scale. A few data indicate that the attack at 750°C was not greatly different from that at 700°C. At 800°C, the rate was much faster, the reaction product was non-adherent, and the rate of scaling did not decrease with time. A combination of the data in table 1 and the curve of figure 5, shows that the nitride coating does not exceed about 0.002 inch thickness after 30 hours exposure at 700°C, but exposure at 800°C converts metal to nitride at the rate of 0.005 inch or more per hour and the process is continuous. Figure 5 is based on a nitride composition of 8.8 percent nitrogen and a density of 18.9 for Tuballoy.

Effect of Alternate Heating and Cooling - At 750°C or 700°C nitride formed was adherent but flaked off to a limited extent when the samples were cooled. To determine if alternate heating and cooling would increase scaling rate, due to exposure of base metal on cooling, samples were heated in nitrogen for a total of four hours at 700°C but were cooled to room temperature in nitrogen at one hour intervals. The results were about 20 percent higher than for a continuous four hour run at this temperature. The actual gain in weight figures, for the continuous and intermittent runs, respectively, were: For RU-557, 4.6 and 5.4 mg/cm²; for M-2, 4.3 and 5.2 mg/cm².

Effect of Oxide Surface on Attack by Nitrogen - The protective action of an oxide surface against attack by nitrogen was found to be negligible. A sample was heated for two hours at 200°C in air, which gave an adherent continuous light oxide film; another was given a four hour exposure and consequent heavier scale. These samples, together with standard cleaned samples, were then exposed to nitrogen at 700°C for four hours. The oxide coatings were apparently readily previous to nitrogen for the gain in weight on coated and uncoated samples was about equal. Specifically, RU-557 with a 2 hour oxide scale gained 5.0 mg/cm² as compared to 4.8 mg/cm² for a clean sample; M-2 with the 4 hour oxide scale gained 5.3 mg/cm² compared

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to 5.8 mg/cm² for the clean sample.

Composition of the Nitride - Complete conversion of the metal to nitride was consistently accompanied by a gain in weight of about 8.8 percent. Analyses of the nitride by the Kjeldahl method just as consistently yielded nitrogen contents of 8.3 to 8.45 percent. Analyses by vacuum fusion yielded results ranging from 7.7 to 9.5 percent. Metallographic examination and vacuum fusion analyses failed to establish diffusion of nitrogen into the metal. Apparently all of the absorbed nitrogen is retained in the nitride crust on the surface of the metal.

The value 8.8 percent, obtained directly from the gain in weight is the most reliable. The assumption that the gain in weight is due to nitrogen, and to nitrogen alone, is justified by the previously discussed evidence of the purity of the nitrogen gas. If the product of the reaction contained oxides as well as nitrides, the gain in weight would be more than the gain in nitrogen, but the gain in weight of samples exposed in purified nitrogen was negligible at 300°C, at which temperature oxygen reacts readily with the metal. Furthermore, re-exposure of samples of the nitride to the furnace atmosphere, for example for 6 hours at 800°C, did not produce any gain in weight, which demonstrates the absence of oxygen. It is concluded therefore that the nitride is free from appreciable amounts of oxide and the gain in weight of the sample is a direct measure of the increase in nitrogen. On the other hand, unsatisfactory results by the Kjeldahl method, for Tuballoy samples with high nitrogen contents, have been obtained here and in other laboratories. It is possible that some nitrogen is lost in the solution process, instead of being completely converted to ammonia. This would lead to low values from the Kjeldahl analyses. The vacuum fusion results are similar to those obtained from samples of other powders; the lack of precision is ascribed chiefly to the spattering and loss of material which usually is encountered in attempts to run samples of powdered material by this method.

A nitrogen content of 8.8 percent corresponds to the formula UN_{1.6}. In spite of the close approximation of this value to the formula U₂N₃, the product probably is a mixture of nitrides rather than a single compound. Reports from Ames (CT 609, 1501, and 1697) recorded compositions ranging from UN_{1.88} to UN_{1.52}, depending upon the temperature and pressure while the nitride was being formed.

The difference in physical form of the nitride produced at alpha or beta temperatures and that produced at gamma temperatures was apparently not related to any difference in composition. Analyses showed the same composition and when the lower temperature black metallic form was heated at a high temperature it was not converted to the gray powdery form. Samples of the nitride powder formed at 800°C or higher temperatures contained particles of the black metallic lower temperature form, evidently formed as the sample was heating and which remained unchanged throughout the course of the run. The black adherent scale and the gray powder apparently are the same nitride but formed at different temperatures or rates.

Oxidation of Nitride - Samples of the nitride powder were heated in air for various times at several temperatures. At 200°C the nitride was only slowly converted to oxide, for after four hours at this temperature the conversion was less than 10 percent complete as indicated by the gain in weight. At 300°C conversion was about 75 percent complete in four hours, while at 400°C or higher temperatures the nitride was almost instantaneously converted to oxide.

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To determine if a nitride scale would afford protection to Tuballoy from air oxidation, one sample was given a light nitride scale by heating four hours at 500°C in nitrogen and was then exposed to air at 300°C for four hours, together with a bright Tuballoy sample. The gain in weight per sq cm of surface of the nitrified sample was 1.8 mg, which represented the net gain in weight when 3.55 mg of oxygen replaced 1.75 mg of nitrogen in the nitride. This was approximately one half of the weight of oxygen picked up by bare metal under similar conditions of exposure. Apparently the nitride coating offers some protection against oxidation, but this protective action occurs only at temperatures below 300°C and is at best a delaying action rather than complete protection.

Specimen Temperatures - Specimen temperatures were measured for an 800°C run by wedging a thermocouple into a slit in a specimen of standard size. The reaction with nitrogen is fairly rapid at this temperature, but the specimen temperature did not rise above that of the furnace to the same degree as was obtained in some of the runs in air. The results were rather inconsistent on several samples, probably due to the large volume of nitride formed which soon insulated the specimen from the thermocouple, but they indicated that the temperature of the specimen at its maximum was not more than 20°C above furnace temperature. The reaction with nitrogen evidently is not as exothermic as the reaction with oxygen.

Summary and Conclusions - The action of purified nitrogen on Tuballoy was studied at temperatures up to 850°C and the following conclusions were drawn:-

- 1) Tuballoy reacted slowly with nitrogen at temperatures up to about 400°C. From 500 to 750°C the rate increased with increasing temperature, but even at 750°C the amount of nitride formation was not serious, corresponding to less than 0.001 inch penetration of the metal in a four hour exposure. Between 750 and 800°C a great change in rate occurred and the reaction proceeded very rapidly at 800°C or higher temperatures and samples 0.06 inch thick were completely converted to nitride in four hours.
- 2) Two physically distinct types of nitride were formed. At 750°C or lower temperatures it was a black, adherent scale with metallic luster; at 800°C or higher temperatures the reaction product was a dark gray, nonmetallic powder.
- 3) The chemical composition of the two forms appears to be the same, their nitrogen content is 8.8 percent corresponding to the formula $UN_{1.6}$.
- 4) There was no significant difference in reaction rate among the different lots of metal studied.
- 5) The nitride was rapidly and completely converted to Tu_3O_8 in air at 400°C or higher temperatures. It was more slowly converted to oxide at lower temperatures.
- 6) A light nitride scale afforded some protection to Tuballoy against oxidation at temperatures of 300°C or lower, but an oxide scale had no apparent effect on rate of nitride formation.

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7) Tuballoy can be exposed to pure nitrogen at temperatures up to 750°C for appreciable periods without serious attack, but at higher temperatures the two react rapidly.

8) The reaction of Tuballoy with nitrogen is less exothermic than the reaction with oxygen. The temperatures of specimens at maximum reaction rate with nitrogen were not more than 20°C above furnace temperature.

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THE BRIGHT ANNEALING OF TUBALLOY

When fabricating Tuballoy rods and wire in this laboratory, process anneals in commercial helium or argon always resulted in excessive oxidation because of the extreme reactivity of Tuballoy with oxygen, nitrogen, hydrogen, and hydrocarbons which are present in small amounts in the commercial gases. It was also frequently desired to bright anneal microsamples of Tuballoy. An investigation of the possibility of bright annealing was therefore undertaken as an adjunct to the scaling tests of the metal in air and in nitrogen. The problem was approached by two methods: (1), annealing in atmospheres of purified helium or argon and (2), annealing in vacuum.

Material and Preparation - For the bright annealing tests, samples about $3/4 \times 1/2 \times 0.060$ inch, (surface area approximately 5 sq. cm.), cut from extruded rod RU-557 were used. This material had the following composition:

C	0.050%
Fe	.005
O ₂	.004
N ₂	.001

The samples were cut directly to thickness with an abrasive cutoff wheel, cleaned on 1-G paper, washed in alcohol and ether, dried in a vacuum desiccator and weighed just before the anneal was started. After the anneals they were reweighed and visually examined for scaling or tarnish.

Bright Annealing in Helium - The furnace used for bright annealing in inert gases, was the same as that previously used for the nitrogen scaling tests, and is shown in figure 1. The tests with nitrogen had shown that simple displacement by the gas being used did not insure removal of all air from the system so arrangements were made for repeated alternate evacuation and flushing with the purified gas. The furnace was preheated in position 1, slid into place over the samples, then at the end of the run back to preheating position to allow the samples to cool in the inert atmosphere. The sample container was an open and silica tube about 0.6 inch inside diameter, small enough to support the specimens on their edges and permit free circulation of gas on all sides of the sample. The rate of flow of the gas during a run was maintained at about 2 liters per hour, and the customary exposure time was four hours at temperature.

Commercial helium usually has a purity of about 99.5 percent. Sufficient impurities were present in gas used directly from the cylinder to result in a weight increase of about 2 mg per cm² for Tuballoy samples exposed for four hours at 400°C. A second sample simultaneously exposed in tandem with the first sample increased in weight only slightly, indicating a "getter" action and removal of a large portion of the impurities by the first sample. Removal of water from the

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helium by drying agents reduced the weight pickup by approximately 50 percent, but there was still a significant weight increase and noticeable scaling.

These results confirmed the opinion that commercial helium could not be used for bright annealing and attention was directed to methods of purification. Figure 1 shows a purification assembly, using activated charcoal at the temperature of liquid air as an absorbent for impurities. This method reputedly gives spectroscopically pure helium. Before each run the charcoal was regenerated by heating slowly to 350°C (in 3 to 4 hours) under vacuum. The samples were introduced into the furnace, the charcoal regenerated as above, and the system maintained under vacuum while the furnace for heating the charcoal was replaced with a Dewar flask containing liquid air. Helium was then introduced into the apparatus and the furnace was alternately evacuated and flushed with the purified helium several times.

Two samples of Tuballoy gained 0.9 and 0.3 mg in weight when exposed for four hours at 400°C to the purified helium. The larger gain in weight was on the first sample in the stream. The impurities in the helium which were reacting with the Tuballoy apparently resulted from recontamination of the gas from the furnace tube or connecting tubes after the purified gas had left the charcoal chamber. Vacuum fusion analyses indicated that the impurity picked up by the samples was largely oxygen. Thus, one sample which as a result of a four hour anneal picked up 0.028 percent impurities by gain in weight, was found by analysis to have increased in oxygen content by 0.027 percent; another sample annealed at the same time but second in the helium stream picked up 0.009 percent impurities and analyses showed its oxygen and nitrogen contents had increased by 0.006 and 0.003 percent respectively.

The "getter" action of the first of two tandem samples suggested the use of a getter tube of Tuballoy turnings in the purification train. This was tried but it was found that getter metal immediately around the specimen still was needed. These results suggested that the purified helium was being recontaminated before it reached the furnace, making it necessary to remove impurities just prior to the contact of the gas with the samples which were to be bright annealed. To accomplish this, the sample container was packed at either end with small pieces of scrap Tuballoy to function as a "getter" for any impurities in the helium which would react with Tuballoy. With this assembly and using charcoal purification, exposures for four hours at 625 and 725°C were made. The samples did not change in weight and true bright anneals were obtained. The "getter" metal was scarcely discolored, possible because the small amount of impurities which it removed were distributed over such a large surface of metal that no visible tarnish resulted. The alpha annealed sample (625°C) emerged with only a slightly "etched" surface, probably due to grain growth, while the beta annealed sample (725°C) was roughened considerably due to the phase change. The surface roughening did not affect the brightness or metallic luster of the samples. Samples annealed in the gamma range for four hours at 925°C showed a marked change in surface appearance with no change in weight. They emerged with a gray, smooth, matte surface, and only when

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the samples were brightened by pickling or electrolytic cleaning was the roughened metallic surface revealed. Some of the characteristics of this film are discussed later in the report.

Figure 2 shows the appearance of specimens annealed at the various temperatures. The contrast among the different samples is greater in the photograph than in the originals and the 925°C annealed specimen appears much darker than its true color. The surface roughening of the 725°C annealed specimen was accentuated by cross lighting in this photograph.

Bright annealed specimens were much more tarnish resistant than were freshly polished samples of Tuballoy. This is demonstrated in figure 3, where photographs of alpha and beta annealed samples immediately after removing from the furnace are shown in the top row, and photographs of the same samples after exposure to the laboratory atmosphere for ten days are shown in the bottom row. A freshly polished sample, marked original, is included; it tarnished to a deep blue color after this same exposure period while the annealed specimens remained bright. This points to a thin protective film of some character formed during the annealing process. These photographs were taken with diffused lighting, consequently the roughening of the surface of the beta annealed sample is not as well shown as in figure 2.

Several attempts were made to determine the nature of the gray surface on the gamma-annealed specimens but the results in general were indefinite. Vacuum fusion analyses of the entire sample did not show any significant pickup of oxygen, nitrogen or hydrogen. Spectroscopic examination of an annealed specimen revealed a "small amount" of silicon which was not present in the original material. The possibility of the reaction of Tuballoy with the silica tube was investigated by annealing a sample entirely surrounded by "getter" metal, the whole of which was placed on tungsten sheet so there was no contact of Tuballoy and silica. After four hours at 925°C, the sample had the usual gray surface obtained in all gamma anneals, demonstrating that the reaction of Tuballoy with silica was not responsible for the change in surface appearance.

In pickling experiments in 60 percent nitric acid, small pieces of the film sometimes separated and floated in the acid, but attempts to isolate enough of these pieces for analysis or diffraction studies were unsuccessful. X-ray diffraction patterns of the coated samples were identical with patterns obtained from the samples in which the gray coating had been removed by pickling. Attempts to study the differences in coated and uncoated samples by electron diffraction were also fruitless.

These experiments show that Tuballoy may be bright annealed in purified helium at temperatures in the alpha and beta ranges but the helium must be highly purified and its purity must be maintained until after it has come in contact with the specimen. Annealing at gamma temperatures in purified helium produced a matte gray surface which was not a tarnish film but could not be called a bright surface.

Bright Annealing in Argon - The argon used for the bright annealing test contained nominally 99.9 percent A and 0.1 percent N₂, but analysis also showed it to contain 0.5 percent O₂. Removal of impurities from the gas by means of activated charcoal at liquid temperatures obviously was not practical for argon. The method utilized for purifying argon consisted of provisions for removing oxygen and water, plus a "getter" tube of hot tuballoy turnings, as is shown in figure 4. The Tuballoy at 800°C should remove all possible impurities except hydrogen, which would be removed by the turnings in the cooler portions of the tube.

As with helium, bright anneals were readily obtained in the alpha and beta ranges when "getter" metal immediately surrounded the samples. In the gamma range an extremely thin matte gray "blush" was produced on annealing in argon, similar to a lightly smoked surface. This appeared to be thinner than that resulting from anneals in charcoal purified helium at the same temperature. The surface roughening could be readily observed through the thin coating and the metallic luster was still apparent. No weight increase resulted when any of the samples were annealed in purified argon. "Getter" metal immediately surrounding the sample was found to be a necessity, when omitted in one run the samples were definitely tarnished and gained 0.2 mg in weight. This again indicated recontamination of the purified gas before it reached the furnace.

The conclusions are the same for argon as for helium. Bright annealing in argon at alpha or beta temperatures is possible provided that the gas is pure when it reaches the specimen. At gamma temperatures alterations of the surface, perhaps heat etching, prevent attainment of a bright anneal.

Bright Annealing in Vacuum - Since the degree of purification of the rare gases to obtain bright anneals in Tuballoy was so critical, annealing in high vacuum was investigated as an alternate method. The furnace assembly was similar in principle to that used for the anneals in helium and argon, that is, the specimens were supported in a silica tube, the furnace tube was evacuated and the hot furnace slid over the samples for the desired time, then removed and the samples allowed to cool to room temperature under vacuum. The first series of anneals was made at temperatures of 625, 725, 825, and 950°C. The vacuum for this preliminary series was supplied by a Hyvac pump and the samples were kept at temperature for two hours. All samples, regardless of the temperature gained practically the same amount in weight (3 mg) and were scaled to a uniform degree.

A mercury diffusion pump was then added to the system, producing a vacuum of about 10⁻⁴ mm Hg in the cold furnace tube. With this refinement bright surfaces on Tuballoy were obtained for two hour anneals in the alpha and beta ranges. In one run of two hours at 950°C, the sample was not tarnished, but gained about 0.3 mg in weight. Subsequent attempts to duplicate this experiment were unsuccessful and specimens exposed at gamma temperatures always became covered with a matte gray film similar to that obtained with purified helium. A section of the sample which

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was untarnished following the 950° anneal was cleaned with emery paper and returned to the furnace for another exposure under identical conditions. The half which had been cleaned became covered with the gray matte film, the other half remained bright. An extremely thin protecting surface was apparently formed under certain conditions which not only prevented tarnish at room temperature but which in this one instance even prevented the formation of the usual matte gray film at gamma temperatures.

The experiments, like the runs in neutral atmospheres, show that bright annealing of tuballoy requires a high degree of purity in the furnace atmosphere. For exposures in the alpha and beta ranges, evacuation to 10^{-4} mm of mercury satisfactorily removes impurities but tarnishing occurs in less completely evacuated systems. At gamma temperatures in vacuum, the surface of the specimen assumed a matte gray appearance, similar to that obtained in purified helium or argon.

Summary - The problem of bright annealing Tuballoy in neutral atmospheres, for example, helium or argon, and in vacuum has been studied and the following conclusions were reached:-

- 1) Tuballoy can be bright annealed in the alpha and beta ranges either in purified argon or helium or in high vacuum. When annealing in neutral gases, the gas must not only be purified, but its purity must be maintained until it comes in contact with the specimen. The ultimate purification was accomplished by utilizing scrap Tuballoy as a "getter" immediately surrounding the sample to be bright annealed. If evacuation is used to produce the neutral atmosphere, the pressure should not exceed 10^{-4} mm of mercury if bright annealing is to be obtained.
- 2) No true bright anneal was obtained in the gamma range. Although no increase in weight was observed in samples annealed at these temperatures in inert atmospheres, a gray matte surface was produced on the samples. The best results were obtained with purified argon, the film was visibly thinner than that resulting from a helium anneal. The nature of the film could not be established by chemical, metallographic, or X-ray methods.
- 3) The surfaces of samples bright annealed in the alpha range took on a slightly etched appearance probably due to grain growth; those bright annealed in the beta range were considerably roughened due to the phase change. This roughening was not associated with any tarnishing or scaling. The surfaces of the gamma annealed samples were found to be rough beneath the smooth matte film when the latter was removed by light pickling or electrolytic cleaning.
- 4) Samples bright annealed in the alpha or beta ranges were observed to be more tarnish resistant at atmospheric temperatures than were newly cleaned samples.
- 5) Bright annealing of Tuballoy, at temperatures in the alpha and beta ranges, can be done on a laboratory scale but would be difficult to apply to large scale or production operations.