AEC RESEARCH AND DEVELOPMENT REPORT

CT-2776
M-C

Contract W-7401-eng-37

PROGRESS REPORT

March 10 to March 17, 1945

METALLURGY DIVISION

Section M-I . . . . . F. Foote

Section M-II . . . . . E. W. Brugmann

Section M-III . . . . . J. H. Chapin

Report Received: March 17, 1945
Issued: March 17, 1945

DISCLAIMER

REPORT FOR WEEK ENDING MARCH 15, 1945

METALLURGY SECTION - FRANK FOOTE, SECTION CHIEF

Total active personnel as of March 15, 1945 - - 36
Academic - - - - - - - - - - - - 24
Non-academic - - - - - - - - - - 12
Transfers in - - - - - - - - - - - - - - - - 0
Transfers out - - - - - - - - - - - - - - - - 0

MI 1.1 - Metallurgy of Tuballoy and its Alloys

Pure Metals: Material deposited on the inner wall of an evacuated quartz tube during the annealing of pure tuballoy metal at 1000°C was identified as TuO_2 and $TuSi_2$.

Tuballoy-Columbium Alloys: During this week, the 2" diameter water-cooled copper mold was used for casting of tuballoy-columbium alloys. A 4% columbium billet was successfully cast at 1400°C, but an attempt to cast a 6% columbium billet failed because of inability to pour the melt due to stopper rod failure. An attempt to cast a 200 lb. rolling billet of 2% columbium-tuballoy failed because the charge could not be heated sufficiently by direct induction. Hereafter, refractory oxide crucibles used in the three-hundred pound micarta furnace will be placed inside graphite inductor shells.

The rates of transformation of single (γ) phase low (1, 2, 4, and 6.5) percent Columbium alloys at 600°C were studied. Samples used had previously been homogenized, recrystallized, and quenched from 1000°C. After the treatments at 600°C the samples were polished, electro-etched in H_3PO_4 solution and examined under polarized light to observe the extent of transformation. In general the rates of transformation were faster than expected. In all the alloys transformation was well begun after 15 minutes (apparently complete in the 1% alloy), and almost, if not, complete after one hour. The 2, 4, and 6.5% alloys transformed at approximately the same rates, yielding grains of alpha tuballoy and very fine two-phase regions as transformation products.

Experiments have been conducted in an effort to arrive at a satisfactory technique for high temperature heat treatments of columbium alloys for X-ray diffraction analysis. Rods filed out of the ingot sections, and powders of the 9% alloy were used. The following observations have been made after heat treating at 1000°C:

1. Although high vacuum (black discharge) was used, TuO_2 was deposited on all quartz tubes and was also found on the specimens.

2. Rods heat treated unprotected in quartz tubes, and also those run in Columbium foil and BeO protecting crucibles seemed to lose tuballoy, the high angle lines being diffuse and noticeably shifted toward the pure columbium positions with increasing time of heat treatment.

3. Rods heat treated in protective tuballoy cylinders gave sharp high angle lines which remain constant in position with increasing time of heat treatment. These rods after treatment, although brightest, have a metallic appearing TuO_2 scale.

4. Powder treated in protective Tu cylinders show diffuse lines.

A rod filed from a 1% ingot was heat treated at 690°C for 16 hours and quenched in water. Only the alpha tuballoy pattern appeared, and the lines were ver

Tensile and hot compression tests were run on specimens cut from the Ames cast thorium billet No. A-39. The piece of metal from which the specimens were cut appeared to be from the top of the billet.

The tensile strengths of two standard 5/16" tensile specimens were 37,000 and 34,000 lbs/sq.in. The specimen which exhibited the lower strength had a porous structure and seemed to contain an unusually large quantity of inclusions. The 37,000 lb/sq.in figure corresponds to the results obtained on a number of other tensile tests which have been run on Ames cast thorium.

Thorium-Beryllium Alloys: Corrosion results of alloys, as cast, in boiling water test, are:

Nominal Composition Wt. % Be	Hours in Test	Weight Change Rate ($mg/cm^2/hour$)
0.4	112	0.005
0.9	112	0.008
1.6 (melt prepared in BeO xible)	112	0.002
1.6 (melt prepared in graphite xible)	112	0.002
2.5	112	0.001

Thorium-Cerium Alloys: Thorium-cerium alloys containing 20.1, 37.0, 57.8, and 84.1 wt % Ce (30, 50, 70, and 90 at. % cerium) have been prepared and examined. The alloys were easily made under argon and there appears to be complete solubility in both liquid and solid states. The microstructures consist of extremely cored dendrites with low melting impurities between the dendrites. The alloys are soft but intergranular cracking causes low ductility. Hot working is limited by susceptibility to oxidation. The alloys will be homogenized to eliminate coring and further cold working tests will be made.

Thorium-Iron Alloys: Filings of the 5.5% Fe alloy were annealed for one week at 725°C and water quenched. The diffraction pattern indicates some solubility of iron in thorium. Lines supposedly of a thorium-iron compound are also present.

Thorium-Silicon Alloys: Corrosion results of alloys, as cast, in boiling distilled water test are:

Nominal Composition Wt. % Si	Hours in Test	Wt. Change Rate ($mg/cm^2/hour$)
1.0	112	0.002
2.0	112	0.002
4.3	112	0.002

Thorium-Beryllium-Silicon Alloys: Approximate corrosion rate loss of the 1% Be, 0.6% Si alloy in boiling distilled water was 0.001 mg/cm^2/hour after 112 hours in test.

MM 3.1 - Metallurgy of Beryllium and its Alloys

Pure Metal: Two beryllium extrusions of 4 to 1 reduction were examined for recrystallization. One was extruded at a ram speed of 9.35 in/sec. and the other at 2.76 in/sec. Neither sample showed recrystallization; both samples were badly cracked.

Tuballoy-Zirconium Alloys: Thermal analyses were made on two specimens of 30 at. % zirconium. No conclusions could be made from the results; either incomplete mixing or concentration gradients are suspected. This work is continuing.

Tuballoy-Columbium-Zirconium Alloys: In order to check the degree of gamma stability in the 6 Zr-2 Cb composition, which originally showed a feather-like structure in the grain boundaries when homogenized and water quench from 1000°C, a small 6 Zr-2 Cb sample was re-quenched from 1000°. The difference in section increased the quenching rate such that the gamma phase was retained.

Also, a recheck on the 8 hour-850°C heat treated samples was carried out (these had been previously quenched from 1000°C and were gamma phase.) Previously the samples were water quenched from the 850° temperature; however, air quenching allowed the gamma phase to transform, producing an increase of 20-25 RC points for all compositions. A complete comparative micro-structure examination on samples quenched by air and water will be completed in the next week.

Metallographic examination of the samples treated for 256 hours at 600°C showed complete transformation for all compositions, evidenced by a lamellar type of precipitation characteristic of an eutectoid.

Corrosion results of the alloys in boiling distilled water test are:

Nominal Composition		Wt. Change Rate (mg/cm²/hr)	
% Zr	% Cb	*A	*B
2	2	0.0004	0.0008-
4	2	0.0003	0.0001
6	2	0.000-	0.0005-
2	4	0.0006	0.0007
4	4	0.0005	0.0005
2	6	0.0003	0.0001

*A-Heat treatment: 256 hours at 850°C and slow water quench; 446 hours in test.
*B-Heat treatment: 256 hours at 725°C and slow water quench; 446 hours in test.

MM 2.1 - Metallurgy of Thorium and its Alloys

Pure Metal: Static Hot Wire-Metal produced from Westinghouse crude thorium, samples before and after working and annealing, was submitted for chemical analysis. The total production for the week was 5.516 grams, all from Westinghouse crude material. Carbon analyses of hot wire metal produced from Ames thorium was 2.4 and 2.5 ppm.

Flow Hot Wire-Two successful runs produced 0.6 grams and 0.5 grams of thorium each. The former was with the stopcock between the mercury diffusion pump and the system barely open and the latter with the stopcock wide open. The flow system is now being completely revamped.

Flow Hot Tube - Using an alundum insert two experiments produced 1.35 grams and 1.48 grams of a brittle metallic appearing material. X-ray analyses gave a good ThO_2 pattern with one extra line. Further experiments will be conducted using a beryllia lined alundum tube. Three thorium extrusions, one 16 to 1 reduction and two 4 to 1 reduction, all extruded at varying temperatures, were examined. The metal contained a large amount of inclusion and foreign structure. As yet no satisfactory polish has been obtained to determine recrystallization.

A light-brown product formed by the action of anhydrous HCl in absolute alcohol on thorium was found to give the same diffraction pattern as white ThO_2 and the various other colored oxides of thorium investigated.

[redacted] CLASSIFIED

MM 4.1 - Metallurgy of Other Metals and Alloys

Static tests on low carbon steel, medium carbon steel, 18-8 stainless steel, and 6% columbium-tuballoy alloy in liquid sodium at 500°C were started on March 10th. The samples will be removed from the test and examined on March 16th. A similar test on aluminum in molten sodium at 300°C was started on March 13th.

Future work on this problem will be directed toward more quantitative tests at higher testing temperatures in liquid sodium essentially free from sodium oxide.

MM 6.1 - Electroplating and Other Coatings

Pretreatment of Thorium: No work was done on this problem during the past week.

Columbium Plating: An attempt was made to produce a columbium compound of intermediate valence by the reduction of pentavalent columbium with metallic magnesium in dilute acid solution. Some reduction probably occurred as indicated by the change in color of the solution. Isolation of the reduced compound was not successful.

A fused melt consisting of equal parts by weight of LiCl and KCl (melting point 400°C) was prepared. The electrolytic conductivity of this melt is very good. A columbium anode corroded very readily with the formation of a light colored insoluble material which permeated the melt. A low melting substance, possibly an alloy of Li and Cu, formed at the copper cathode and dropped off into the bath. After electrolyzing for a short time a piece of iron was substituted for the copper. Continuing the electrolysis lead to the deposition of copper on the iron cathode. No columbium was deposited.

Beryllium Plating: A rolled steel handle was tried as a support for slugs. The slug did not fall off during plating (745°C) but evidence of deterioration of the steel-tuballoy junction was noted. A copper handle failed after a few minutes at 915°C. The use of 120 mil tungsten wire is being investigated.

Cursory experiments on the corrosion of extruded $\frac{1}{4}$" beryllium rod in the beryllium plating bath, the latter being maintained at a dull red heat, produced the following results:

1. An area of roughly 2/3 sq. in of Be lost 13.2 mgs. in 30 mintues. Gassing was observed at the Be surface and a loose, black powder formed on the surface of the metal.

2. Anodic corrosion of Be (copper cathode) showed an apparent anode efficiency of 135%. Gassing was observed at both electrodes and a black powder formed on the Be surface.

Beryllium oxyfluoride softens but does not melt as the temperature is raised; thus the use of this salt alone is not satisfactory for plating purposes. The furnace being used for the beryllium plating work was damaged when some of the melt spilled out of the graphite crucible and came in contact with the alumdum furnace core. This accident held up work on this problem during the past week.

A $\frac{1}{2}$ W-slug was Be-plated in the gamma range. The plate was discontinuous but in places where there was plate the thickness was consistently 0.3 mils. There was a dark line at the interface. The beryllium itself was fairly clean. No diffusion of beryllium into tuballoy could be detected.

A second $\frac{1}{2}$ W-slug was plated in the alpha range. There was very little plate found. Where there was plate the thickness ranged from 0.05 to 0.1 mils and there was a very heavy dark line at the interface.

[redacted]

MM 7 - Service

1. Two silver coated glass tubes were plated with copper for Dr. Shaw in Kearsons.

2. Two 2" rods of thorium were plated with 0.005" of copper for H. Bothke of the Fabrication Section.

3. Two copper electrical connectors were silver plated for the electricians.

4. A brass counter chamber was plated with copper and another was platinum plated for Miss Burke of the Instruments Section.

5. A piece of titanium was copper plated for Joe Lane of the X-ray group.

[redacted]

E.W.Brugmann, Section Chief

Corrosion Section	Report for Week Ending March 14,1945
Active Personnel as of March 14, 1945	37
Academic	18
Non-academic	19
Transfers in	0
Transfers out (Wilma Potts, Tobbie Zion)	2

MM 1.2 - Tuballoy and Alloys

The following tests on tuballoy alloys were run in boiling distilled water. All samples had been hot rolled and then heat treated two hours at 850°C, followed by a water quench (heat treatment No.1). Data on the 4% Cb alloy, especially at the short exposure times, are considered to be less reliable than the others.

Alloy No.	Nominal Composition by Weight	Weight of Metal Lost (grams)	Weight of Metal Lost (mg/cm^2)	Uncertainty in Weight loss due to Cleaning Procedure Estimated from cleaning curve (mg)	Time on Test hrs	Average rate of metal loss from start of test $mg/cm^2/hr$
1,1	6% Cb	7.3	0.58	24(1)	193	0.003±0.001
1,2	4% Cb	4.6	0.48	not determined(2)	24	0.02
		9.5	0.96	not determined(2)	48	0.02
		7.3	0.72	not determined(2)	102.5	0.007
1,3	2% Cb	1.4	0.17	0.1(3)	24	0.007
		2.1	0 24	0.1(3)	48	0.003
		11.5	1.34	0.4(3)	191	0.007

(1) Cleaned with 40% HNO_3 at 26°C
(2) Cleaned with 30% HNO_3 at room temperature, criterion of clean sample is loss of colored film.
(3) Cleaned with 25% HNO_3 at room temperature.

A specimen of alloy 1,1 (6% Cb, heat treated two hours at 850°C, WQ) was tested in a 1% solution of sodium chloride, heated in the steam autoclave at 125 lbs/sq in. steam pressure. The weight loss in one day was 0.06 mg/cm^2 and in two days was 0.17 mg/cm^2 as determined on a specimen from which the corrosion product was not removed. The weight loss measured in the same way on alloy 1,1 in distilled water in the autoclave under the same conditions has been reported as 0.03 mg/cm^2 (after two days) and 0.00 mg/cm^2 (after four days).

At 3°C, 40% nitric acid gave a cleaning curve on a corroded specimen of alloy 1,1 in which, after a small but rapid initial loss, the rate of weight loss continued to increase with time for the five hours tested. Alloy 1,2 under the same conditions showed a point of inflection between the slower oxide removal (following rapid initial reaction) and the somewhat higher rate at which the very nearly clean metal went into solution. In general the rate thought to be characteristic of the nearly clean metal for the 6% and 4% columbium alloys sometimes increases with time and sometimes

does not. Alloy 1,1 cleaned in 10% nitric acid at a temperature of 84 ± 2°C, also gave a cleaning curve with such a point of inflection. Neither type of cleaning curve is as valuable as the simple curve in which the rapid initial rate of weight loss decreases quite sharply to a distinctly smaller constant value.

Limits of uncertainty in the metal weight loss can be determined objectively in the case where a point of inflection is found (though they are wide in this case). In the case where the rate of weight loss continually increases, the decision as to when the sample is clean depends more upon the appearance of the sample than on the actual cleaning curve. More suitable cleaning agents are sought.

MM 2.2 - Thorium and Alloys

An 813 hour test has been completed on Thorium alloy containing 0.6% tuballoy in aerated water flowing at 20 ft/sec containing 20 ppm Ca^{++}, 6 ppm Mg^{++}, 85 ppm $SO_4^{=}$, 1 ppm Cl^-, ~ 5×10^{-3} N H_2O_2 at 70°C, pH 6.3. As reported last week, the average weight change of the three uncleaned specimens was 17.5 mg/cm^2/hr loss. After cleaning, the samples showed an average rate of metal loss from the start of 23.8 mg/cm^2/hr.

MM 3.2 - Beryllium and Alloys

Beryllium exposed seven days in NaCl solution at 70°C and atmospheric pressure undergoes weight change (samples cleaned with 25% HNO_3 at room temperatures) as follows:

ppm Cl^-	In Oxygen Free Solution	In Oxygen Saturated Solution
1	0.05 - 0.10 gain	0.05 - 0.035 gain
5	0.05 - 0.10 loss	0.03 - 0.04 loss
10	0.08 - 0.10 loss	0.05 - 0.07 loss
1,000	0.08 - 0.09 loss	3.46 - 4.44 loss
10,000	0.11 - 0.13 loss	6.2 - 6.1 loss
30,000		9.0 - 9.5 loss

MM 4.2 - Other Metals and Alloys

The upper temperature at which 2S aluminum can be used in contact with distilled water is near 270°C. Samples of bar stock were exposed in deaerated distilled water in pyrex lined bombs, as indicated below:

8W16

Temperature (°C)	Corresponding Saturated Steam Pressure (lbs/sq in)	Time (hours)	Result
211	281	18	Slight attack
215	306	16	Slight attack
219	330	14	Slight attack
271	815	20	(Complete)
302	1277	12	(disintegration)

Aluminum in contact with iron in distilled water for thirteen hours at 200°C was only slightly attacked. The extent to which silica is leached from the pyrex bomb liners has not been determined.

The amount of silicon in water boiled at 100°C in a quartz (vireosil) flask is reduced when aluminum is present:

Time (hours)	Quartz + Water pH	Quartz + Water SiO_2 (ppm)	Quartz + Water + Al pH	Quartz + Water + Al SiO_2 (ppm)	Aluminum (grams)
0	6.6	0.5	6.6	0.5	4.3930
24	6.9	1.4	6.8	0.6	4.4003
41.5	6.9	2.8	6.8	0.7	4.4051
59	6.9	5.6	6.7	1.4	4.4051
77	6.7	10.5	6.6	2.4	4.4033
110.5	7.0	12.4	6.9	3.0	4.4033
127.5	7.1	14.3	7.0	3.5	4.4035

MM 9.2 - Survey Volume

First drafts of the tables on tuballoy alloys have been prepared.

Analytical

The number of solution constituent determinations performed by the analytical laboratory during the past week follows:

Tuballoy and Alloys, MM 1.2	7
Other Metals and Alloys MM 4.2	230
Others	7
Total	244

9W16

Report for Week Ending 3/16/45
Fabrication Section — John H. Chapin, Section Chief

Active Personnel as of 3/16/45

Total	10
Academic	8
Non-Academic	2
Transfers In	0
Transfers Out	0

MM 1.3 - Fabrication of Tuballoy and its Alloys

Production of good epsilon rod by extrusion has not been successful. Attempts at extrusion of epsilon on Wolverine's press were made on 3/15, but information from the trial is not available as yet.

The cast slugs from N.B.S., after being straightened on the Medart at Joslyn, have been measured for warp; an average warp of less than 10 mils was found. The straightening operation also gave an average decrease in slug diameter of 5 mils. Two slugs are being sectioned longitudinally; five slugs are being machined in steps of twelve mils, each slug being mapped for defects after each cut.

MM 2.3 - Fabrication of Thorium and its Alloys

A section of a Th-Ce-Be alloy (22% Ce, 1.6% Be, 76.4% Th) was forged at room temperature, breaking after 1-2 light blows. This alloy heated appreciably during the hammering. A second section of this alloy was forged at 604°C; this piece broke after one hammer blow. Further forging on the broken sections produced a shower of sparks, and deep edge cracks in the material.

A comparative study of Westinghouse and Ames material is underway; data on hardness, hot and cold rolling, annealing, forging, swaging, and coating will be taken.

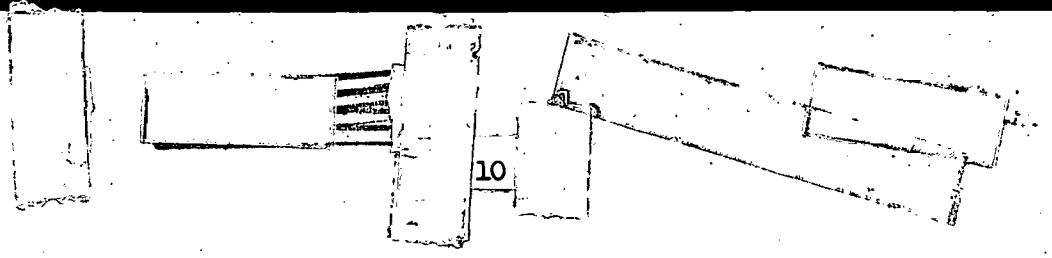
Extrusion of thorium billets into 3/4" and 1/2" rods was accomplished on the Wolverine press, but further information is not yet at hand.

MM 3.3 - Fabrication of Beryllium and its Alloys

Attempts were made to swage extruded 1/2" rod at 1200°F through a 3/8" die. Rods cracked badly.

A Be extrusion billet was copper plated with 2-5 mils of copper, heated to 800°C, and extruded through a 30° 1/4" die. Approximately 3/4 of the billet extruded before freezing in the die; the extruded rod was smooth. Plating will be investigated further, as copper cans tend to alloy with Be at elevated temperatures.

10274



Extrusion of various diameters of Be rods was accomplished at Wolverine, but data are not available.

MM 8.3 - Equipment

Continental Forge & Machinery Company, East Chicago, Illinois, has agreed to machine the roll blanks obtained from Joslyn to our drawings and specifications.

11 10 14