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CT-2700

PROGRESS REPORT

I

on

METALLURGY OF TUBALLOY

to

UNIVERSITY OF CHICAGO

from

BATTELLE MEMORIAL INSTITUTE

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SUMMARY OK

The thermal conductivity of thorium, as extruded, gave values 10 to 15% higher than tuballoy in the temperature range of 100 to 350°C. with a lower temperature coefficient.

Annealing of cold-rolled thorium strip (Ames) showed partial recrystallization in one-half hour at 700°C. which became substantially complete in one hour, giving fine equiaxed grains. The one-hour anneal at 700°C. gave minimum hardness of 121 VDH (87 R_e). Higher temperatures increased the grain size and gave somewhat higher hardness values, indicating a precipitation effect which gave indications of overaging at 1100°C.

No dipping processes have been found which remove scale or oxide from thorium. Very satisfactory cleaning was obtained on certain types of scale with anodic pickling in phosphoric or phosphoric-sulfuric acids.

Vacuum-fusion oxygen analyses give values of .011 to .04% oxygen for Ames metal and .152 to .168% oxygen for Westinghouse thorium.

Microscopic and X-ray evidence is presented, indicating that thorium forms an unstable carbide and probably stable mono- and dicarbides.

X-ray studies of scales on thorium show that they consist largely of the oxide, but a thin black scale has not been definitely identified.

Tentative data have been obtained on the thorium-hydrogen system and indicate a hydride having the formula $ThH_{3.56}$. Westinghouse metal formed hydride rapidly at 210 to 220°C., but Ames metal reacted very slowly. end

Dilatometer studies on the Cb-Tu alloys were completed, showing that the beta field disappears at about 3% Cb as compared with 2% for Mo. Thermal-conductivity measurements on the 4% Cb alloy in the as-received condition gave values between those for pure metal and the 5% Mo alloy.

/ Ti~~tanium~~ appears to lower the ~~beta-gamma~~ β-γ transformation, but the alpha-beta transformation in Ti-U alloy is but little affected. Corrosion tests in distilled water on 2.3% Ti-~~tuballoy~~ U alloy show about one-fourth the rate of attack as for pure metal. /end

Additions of 5 and 10% indium to tuballoy gave inhomogeneous alloys containing more than one phase.

Investigation of the rolling of aluminum containing tuballoy indicates that alloys containing up to 18% Tu can probably be rolled commercially. Alloys with 18 to 30% Tu were rolled experimentally, but it is doubtful that they would be tolerated in a commercial shop because of high pouring temperatures and difficulties in fabrication. Tests on making Tu-aluminum alloys with additions of tuballoy oxide show 50-60% recovery of Tu when using a cryolite slag on the bath. Further tests are in progress on other methods.

The thermal conductivity of pure tuballoy was determined for temperatures of 100 to 350°C. for comparison with the results obtained on the Mo and Cb alloys. The results show .272 and .318 watts/cm./°C. for temperatures of 150 and 300°C., respectively.

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An X-ray pattern for beta tuballoy has been obtained on specimens prepared from a .6% Mo alloy. Dilatometer and X-ray studies confirm that beta can be retained at room temperature by quenching this alloy.

A summary report on the tuballoy-nitrogen system is being prepared. Some of the conclusions from this work are summarized in the present report.

EXPERIMENTAL DATA

Properties of Thorium

Thermal Conductivity OK

The thermal conductivity of a sample of extruded Ames thorium was determined for the range of 100 to 350°C. in the as-received condition. The results are given in Figure 1, where a comparison with tuballoy may be made. The results on thorium were obtained on subsize specimens and are thus subject to more error.

The conductivity of thorium appears to be 10 to 15% higher than tuballoy in this temperature range and shows less change with temperature.

Annealing of Cold-Rolled Thorium OK

A section of the 0.5" extruded Ames metal was cold rolled to 0.058" strip, annealing it one-half hour at 1000°C. three times in the process. Some edge cracking was observed, but it was not excessive and probably was partially caused by the starting shape of the sample. The final cold reduction was 61%, and the hardness as-rolled was 107 Rockwell E (1/8" ball, 100 kg.), or 177 Vickers (10 kg.).

The cold-rolled strip was cut into sections and a section annealed one-half hour at each of the temperatures shown in Table 1 in an atmosphere of argon. The scale formed was removed by abrading, the hardness measured, and

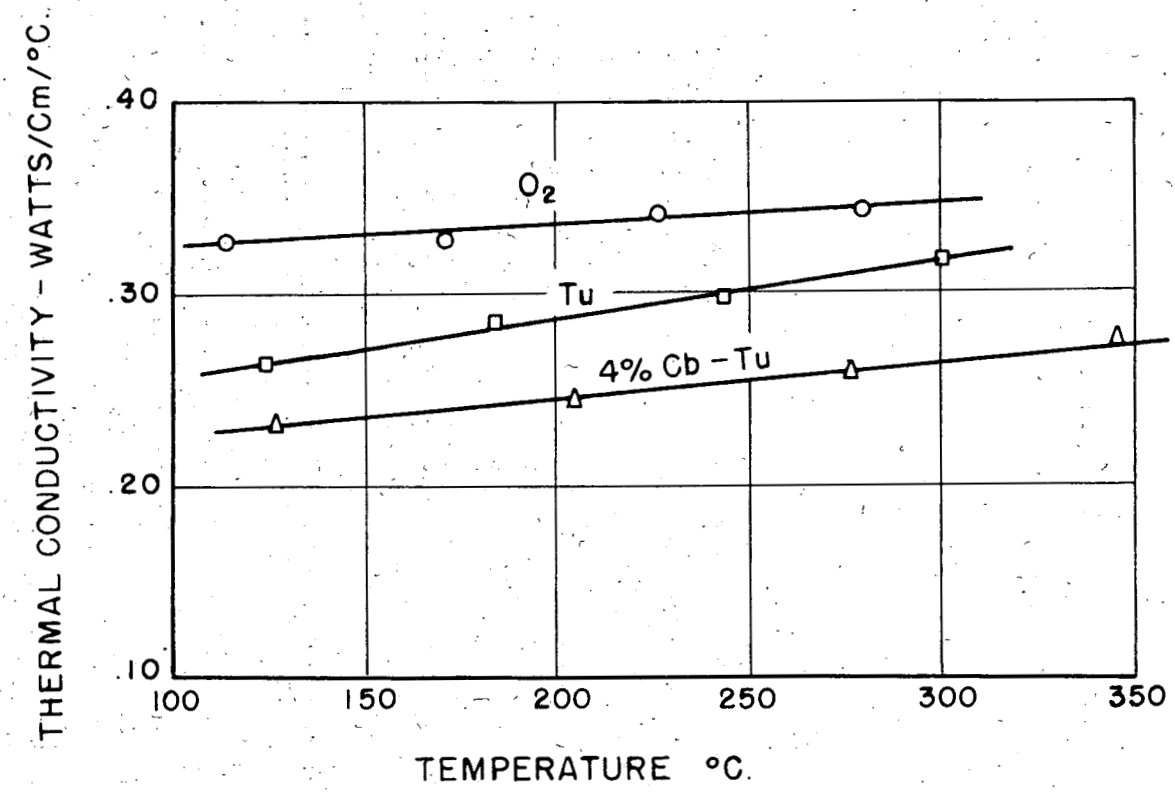

FIGURE 1 - THERMAL CONDUCTIVITY MEASUREMENTS

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0-410

TABLE 1. HARDNESS DATA ON ANNEALING 60% COLD ROLLED TH. STRIP

Annealing Temperatures	1/2 Hour		1 Hour		2 Hours		6 Hours	
	10 Kg. Vickers	Re*	10 Kg Vickers	Re	10 Kg. Vickers	Re	10 Kg. Vickers	Re
As Rolled	177	107	-	-	-	-	-	-
500°C.	154	102	152	102	146	100	-	-
550	150	99	146	99	143	98	-	-
600	145	99	136	97	133	95	-	-
700	128	88	121	87	123	88	-	-
800	128	91	133	90	131	90	-	-
900	135	92	134	95	135	92	-	-
1000	136	-	138	94	136	93	-	-
1100	133	93.5	129	92	-	-	126	-

* Rockwell E
1/8" ball, 100 Kg. Load.

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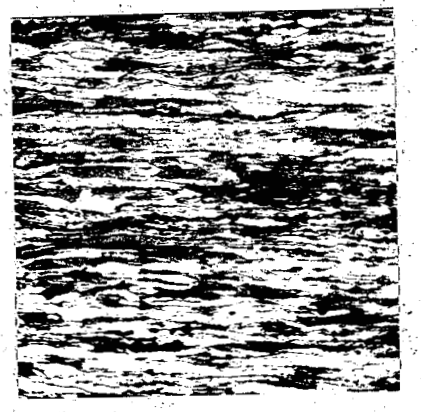
the microstructure noted. The samples were then heated for an additional one-half hour and one and one-half hours at the same temperatures, and the hardness measured after each period. Table 1 summarizes the hardness values obtained.

The structures obtained on the samples annealed for one-half hour are shown in Figure 2. The as-rolled strip showed the typical elongated grains of a severely worked metal. Annealing at 500°C. and 550°C. produced no marked changes. The sample annealed at 600°C. showed no change at the end of one-half hour, but recrystallization had started after one hour. There was partial recrystallization apparent in the sample heated one-half hour at 700°C. and more complete recrystallization in one hour at this temperature. As the temperature was increased from 800°C. to 1100°C., there was a corresponding increase in grain size. Heating an additional five hours at 1100°C. did not increase the grain size appreciably.

Apparently the small equiaxed grains obtained in one hour at 700°C. produced the softest metal. The slight increase in hardness at higher temperatures appears to result from some precipitation effect.

This sample of material was much harder, both as rolled and after annealing, than the Westinghouse compacted metal tested last month. The hardness of the latter as cold rolled 60% was only 83 R_e, which was less than the minimum obtained on annealing the Ames sample. As reported last month, data were only approximate, but, even on that basis, there appeared to be a marked difference in the hardness level between the two lots of material. This difference in hardness probably relates to the method of preparation of the Westinghouse metal and its processing prior to rolling.



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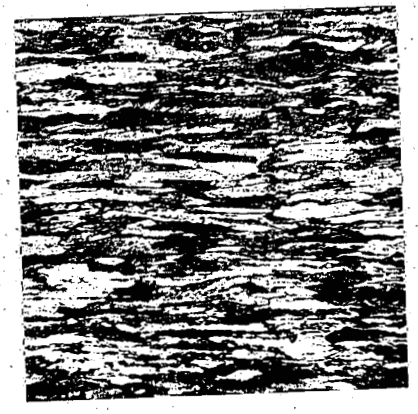
As rolled.



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500°C.

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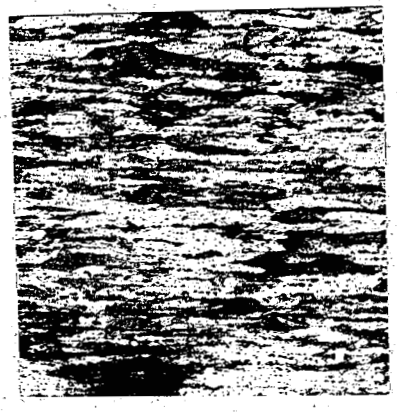
550°C.



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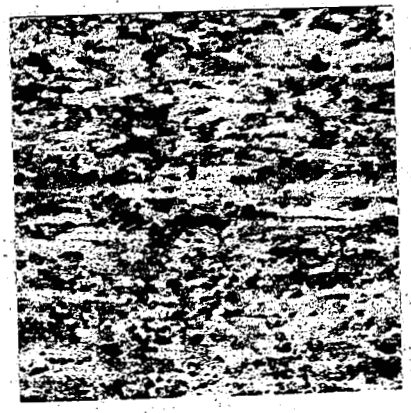
600°C.



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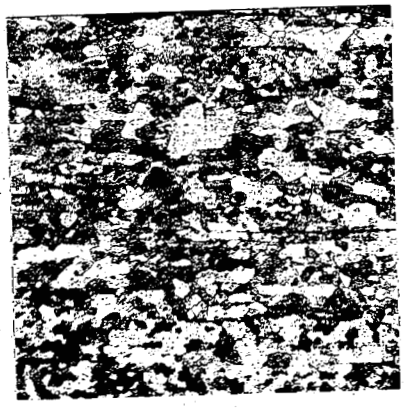
700°C.



34356

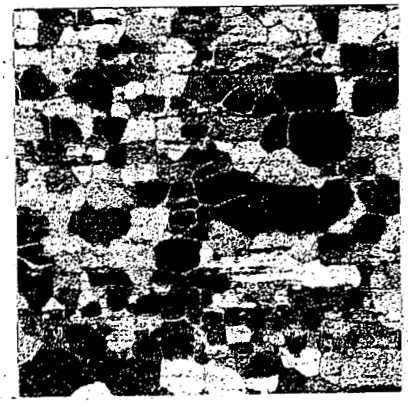
800°C.

34357

900°C.

34358

1000°C.



34359

1100°C.

Figure 2. Structure of cold rolled strip annealed 1/2 hr. as shown. Electrolytic etch. 100X.

633

Pickling

Acid Dips It was desirable to have a pickling procedure available for the removal of fabricating and heat-treatment scales from thorium surfaces. Preliminary experiments indicated that the type of scale, as determined by its manner of formation, definitely affected its ease of removal. For example, scale formed during extrusion or by heating the metal in an open flame has not been satisfactorily removed by any of the procedures tested. On the other hand, a scale developed during standing of cold-rolled, annealed surfaces was quite readily removed by the electrolytic procedures described below. The shiny, black scale formed by cold-rolling of annealed specimens was transformed into a bulky, gray scale on standing overnight. Some of this was easily rubbed off, but the rest adhered to the metal surface requiring removal by other means.

Ordinary immersion in acids or alkalies did not visibly attack the gray scale. A slight evolution of gas was observed in some instances, with no other apparent effect. Concentrated hydrochloric acid vigorously attacked one of the specimens, resulting in a black layer. Exploratory dips in concentrated HNO_3 and in a ferric sulfate - hydrofluoric acid mixture changed the color of the film to yellow, but did not remove it. A subsequent dip in aqua regia removed the film, exposing a bright metallic surface. The latter combination of etching dips were not readily duplicated, however, and further immersion in aqua regia caused the formation of another black film. Therefore, the procedure was not considered practical, and further experiments were mainly concerned with electrolytic pickling.

Electrolytic Pickling Consistently good removal of the gray scale was obtained by anodic treatment in solutions of phosphoric acid, or in mixtures

containing phosphoric acid. No attempt was made in these preliminary tests to define limits of solution concentration or of other operating variables. Anodic treatment for about one to five minutes at 1 amp./sq. in. in the following mixtures was generally sufficient to remove the gray scale completely and to expose a semibright metallic surface. Solutions containing phosphoric acid alone and with additions of acetic and sulfuric acids and water were tried as follows:

H_3PO_4, cc.	H_2SO_4, cc.	CH_3COOH, cc.	H_2O, cc.
60	0	0	0
30	0	0	30
30	30	0	0
30*	30	0	20 to 110
40	0	40	40
40	10	40	40
20	10	10	40
0	18	111	dil. to 200
10	20	10	40

* Preferred solution because of more uniform current flow.

Anodic treatment in concentrated phosphoric acid generally produced a brighter and whiter surface, approaching an electropolished appearance, but the procedure was somewhat difficult to control because polarization effects interfered with maintenance of a uniform current density. The solutions containing both sulfuric acid and water in addition to phosphoric acid were more conducting and easier to control. The metallic surface exposed was somewhat more frosty in appearance, but the gray scale seemed to be completely removed. A precipitate was formed in all of these solutions after a few pieces had been anodized in them.

OK

Molten-Salt Dips. Zinc - ammonium chloride over molten zinc permitted obtaining a hot-dip zinc coating on abraded thorium. The flux, however, did not appear to give a uniform cleaning action, and zinc chloride by itself did not give a coating.

The ternary LiCl-KCl-NaCl eutectic had a similar action, but permitted hot tinning of thorium in a molten bath.

Stannous chloride when heated in contact with the metal liberated tin, but did not give an adherent coating.

Oxygen Content of Extruded Thorium as Determined by Vacuum-Fusion Analysis

OK

One vacuum-fusion extration was made at 1850°C. on Ames metal. Although the extraction appeared to be complete in 30 minutes, subsequent runs showed the necessity of operating at higher temperatures in order to recover all of the oxygen, and all other runs were made at 2000°-2100°C. Several methods of handling the melt were tried. The most satisfactory results were obtained by dropping the metal into a graphite crucible containing a loose covering of granular (1/8") graphite (one particle deep) on the bottom. The sample melted and ran between the particles, thus providing better contact of metal and graphite. Before dropping a second sample, a similar monogranular layer of graphite was dropped and outgassed.

Deep die scratches, or folds, in the surface of the extruded Ames metal rod made sampling difficult. About a 1/16" layer was removed from the surface of the rod to eliminate imbedded particles, but it was not certain that all foreign material was removed. This may account for some of the differences found from sample to sample. The Westinghouse rod had a better surface, and satisfactory samples were readily prepared.

Extraction appeared complete for the Ames metal in 30 minutes to one hour, while 90 minutes to two hours were required for the Westinghouse metal.

Table 2 contains the results obtained on several samples of each metal. Samples of Ames metal yielded .011% to .040% oxygen, while the Westinghouse metal analyzed .152% to .168%. Segregation, particularly in the

TABLE 2. VACUUM FUSION ANALYSIS OF EXTRUDED THORIUM

Weight of Sample in Grams	Source	Extraction Temp.,°C.	Extraction Time in Minutes	Wt., Per Cent Oxygen
3.2	Ames	1850	30	.011
3.6	"	2100	30	.040
6.2	"	2000	45	.020
5.5	"	2110	30	.014
4.8	"	2110	60	.024
5.4	Westinghouse	2000	90	.168
7.3	"	2000	90	.157
4.5	"	2060	120	.166
5.4	"	2060	120	.152

case of the Ames metal, is believed to be the principal cause of the variation in the analytical results.

With the analytical procedure described above, practically the entire melt is converted to a solid carbide as the carbide-forming reaction progresses slowly from the edge of the melt toward the center. In some of the earlier melts, only about one-fourth of the metal became carbide, but metallographic examination of the remaining metal revealed that the original stringers of oxide had disappeared. This observation supported the belief that the reduction of the oxides was complete.

Blanks amounted to 10% of the total CO collected from the Westinghouse metal and 20-30% of that for the Ames metal. However, the blanks were quite consistent, and possible error caused by variation in blank would amount to no more than ±.002%. Measurement in the Orsat may introduce an additional error of ±.002% on samples of the size used in these analyses. Thus, the precision of the method appears to be about ±.004% on a five-gram sample.

Small amounts of nitrogen were recovered from the samples. Although the values were erratic, the results indicate that Ames metal contains about .002% nitrogen compared to .007% for Westinghouse metal.

Carbide Formation in Thorium

The small residues of thorium remaining after a vacuum-fusion oxygen analysis were examined microscopically to investigate the carbides formed. Since these samples were melted in graphite crucibles, the carbon content of the residue should have been relatively high.

One sample adhered to the bottom of the crucible. A cross section of the interface between the crucible and the metal is shown in Figure 3. There was a large massive carbide phase adjacent to the graphite, showing a diffusion

34471

Figure 3. Cross section of the interface between graphite crucible and the thorium carbide remaining after vacuum-fusion analysis. Mechanical polish. Air etch. 100X.

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zone with the inner section, which appears to be largely the stable-carbide phase, shown as globules in Figure 4. The massive carbide was extremely fragile and decomposed, on exposure to air, into a mixed yellow and white powder a few hours after the vacuum-fusion melt was made. The surface was photographed immediately after polishing under carbon tetrachloride before much hydrolysis could occur.

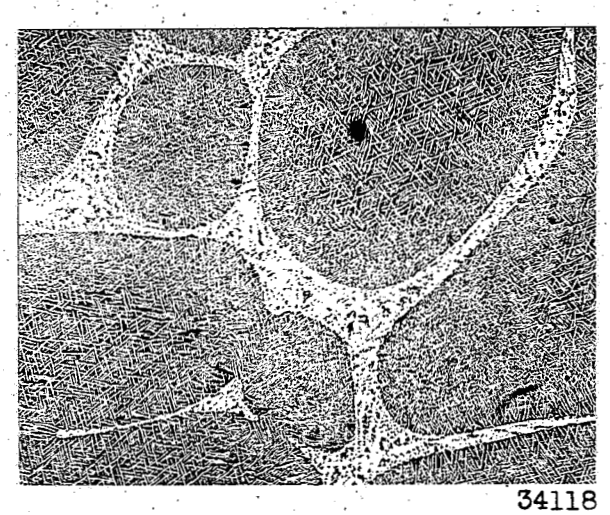
In Figure 4 another type of carbide structure is shown. This too was obtained from an oxygen-analysis residue. The sample shows large, round globules outlined by a eutectic phase. The globules appear to have a Widmanstatten structure, indicating the possibility of two carbides, perhaps mono- and dicarbides, combined to form a sesquicarbide.

Some of the yellow-white powder was examined by X-ray diffraction and found to give a very diffuse pattern of ThO_2, a face-centered cubic structure with a_o=5.60 A. On heating to 300°C. in air, the powder turned white and gave the same pattern with very much sharper lines. The stable, metalloid-appearing, central portion of the vacuum-fusion residue gave the diffraction patterns of two face-centered cubic phases, one with a_o=5.29 A., the other with a_o=5.85 A.

It may be theorized that three carbides exist: (1) an unstable acetylide, ThC_2, presumably isomorphous with CaC_2; (2) a stable form of ThC_2 with a face-centered cubic structure, possibly CaF_2 type, with a_o=5.85 A.; and (3) ThC with a face-centered cubic structure, a_o=5.29 A. These speculations are to be tested in further studies.

X-Ray and Electron Diffraction Examination of Thorium-Oxide Scales

During the course of rolling and annealing small pieces of thorium, it was observed that the thin, black, adherent scale gradually turned to a



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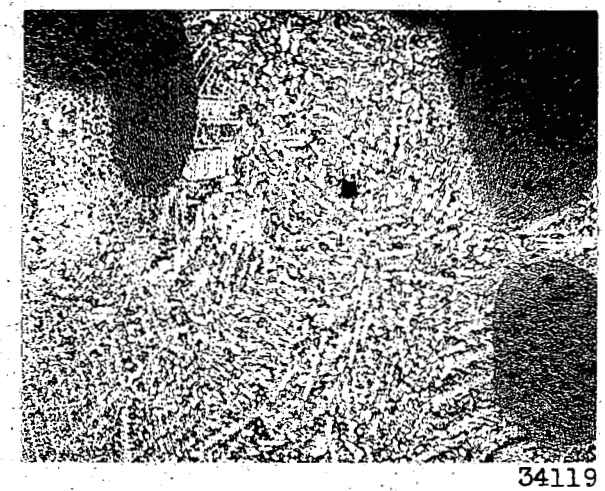

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Figure 4. Structures of stable carbides in residues of vacuum-fusion oxygen analysis. Mechanical polish. Iodine etch. 250X.

gray, loosely adhering powder on exposure to the atmosphere. Immediately after rolling, a small strip of metal was cut into four pieces. One piece was examined by electron diffraction immediately. The other pieces were stored (a) in a desiccator, (b) in air at 50% relative humidity, and (c) in air at 95% relative humidity. It was found that the rate of formation of the gray powder was greatly increased by the presence of moisture in the air. The gray powder always gave the diffraction pattern of ThO_2 (F.C.C., a_o=5.60 A.), although in some cases a fainter pattern (F.C.C., a_o=5.21) was also present. The adherent black scale has not yet been adequately examined. An electron diffraction photogram from one sample gave a ThO_2 pattern, plus a much stronger pattern of a face-centered cubic phase with lattice constant of about 5.8 A. Another piece that had been annealed in argon after rolling gave only the pattern with a_o=5.8 A. It is possible that this phase is the carbide with a_o=5.85 mentioned in the preceding section and was formed by reaction of oil from the rolls during annealing. In any case, electron diffraction is too sensitive to thin superficial films to give satisfactory information about the composition of the black scale. Further study with X rays is in progress.

Thorium-Hydrogen System

Studies of the formation and composition of thorium hydride are in progress. The data obtained up to the present time are rather discordant and must be considered as purely tentative.

The experimental method consists of determining the composition of hydride by volumetric measurement of the hydrogen that reacts with a known mass of metal. The apparatus is similar to that used in the study of the tuballoy hydride.

Freshly cut chips made on a shaper were introduced into the reaction chamber without further treatment. The system was then sealed and evacuated as rapidly as possible. The furnace was brought to temperature and hydrogen added to form the hydride.

Using Westinghouse metal (section with ends numbered 5-6; 5 end), the reaction started rapidly at 219°C. and was carried to completion (at 219°C.) with very little slowing of the rate, except for the last few (about 14) milliliters of hydrogen. The hydrogen was absorbed at about 6 ml. per minute by 2.5 g. of metal. A composition of $ThH_{3.57}$ was obtained at this temperature. As a check, the temperature was raised to 294°C. where the composition was practically the same, $ThH_{3.56}$. If the correct formula is ThH_4, it would appear that approximately 10% of the metal failed to react with the hydrogen. This is nearly 10 times as much metal as can be accounted for on the basis of oxide as determined by vacuum-fusion analyses.

Part of the hydrogen was removed from the system, and the decomposition pressures at various temperatures determined. In Figure 5, Log P is plotted against the reciprocal of the absolute temperature. From this curve, the heat required to decompose one mol of ThH_4, according to the following equation, was calculated:

$$ThH_4 \rightleftharpoons Th + 2H_2; \quad \Delta H + 29{,}500 \text{ cal./mol}$$

Failure to reach equilibrium may account for deviations from the Log P vs. 1/T plot shown in Figure 5, inasmuch as all points lying above the line were approached from higher pressures and all points below the line from lower pressures.

Experience has shown that both the decomposition reaction and the synthesis reaction are extremely sluggish under certain conditions. Point No. 5, which was recorded after a period of 42 hours, indicated a decomposition pressure

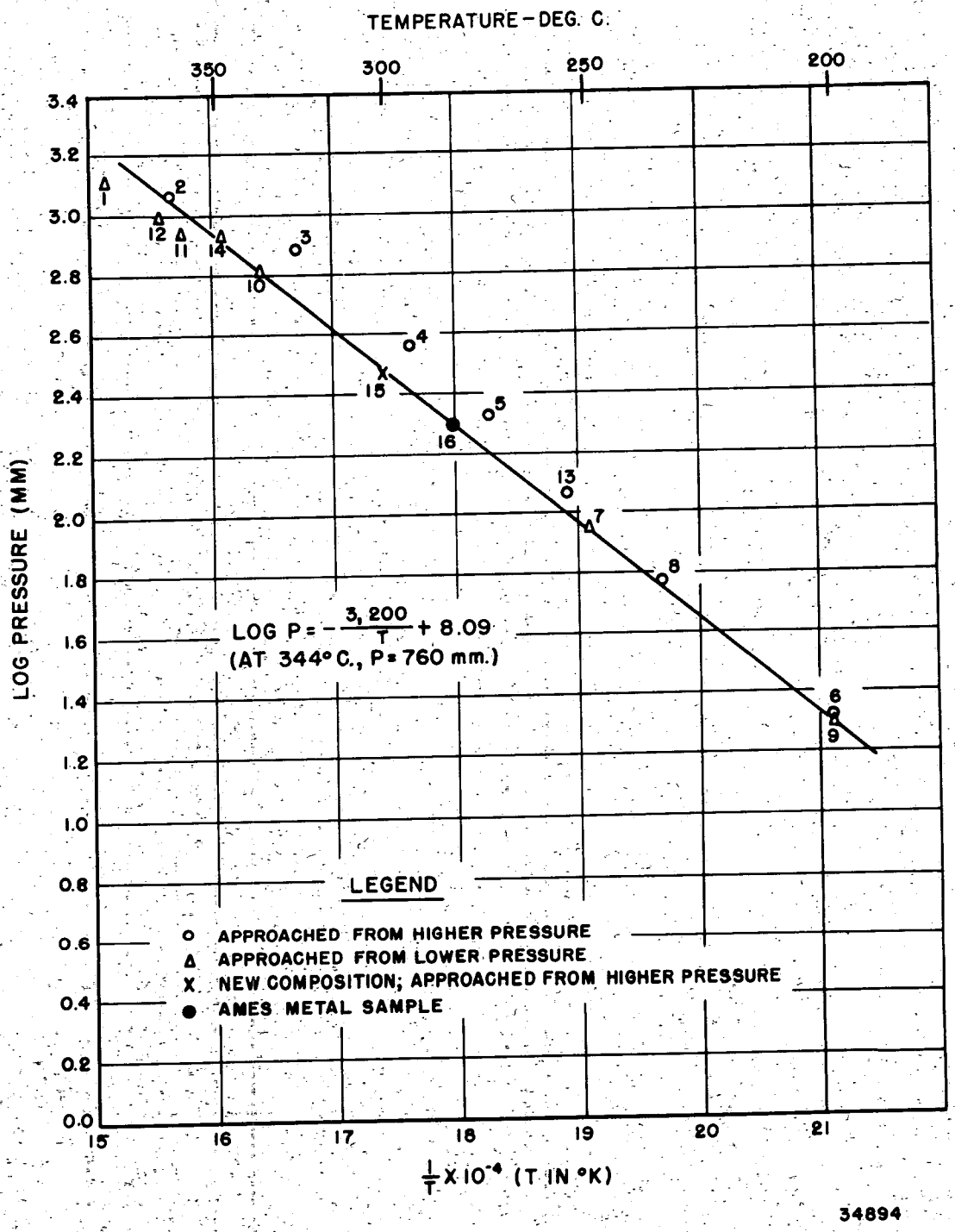

Figure 5. Equilibrium pressure as a function of temperature for the system

$$\text{Hydride} \rightleftharpoons \text{Thorium} + \text{Hydrogen}.$$

Except for Point No. 16, the data were all obtained on a single sample of Westinghouse metal.

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of 215 mm. at 274°C.; whereas, the plotted value at that temperature is 160 mm. Point No. 6 at 201°C., on the other hand, reached the indicated equilibrium pressure in three hours. Since it would normally be expected that equilibrium would be reached more rapidly at higher temperatures, this is difficult to explain.

The average deviation in furnace temperature was ±1.0°C. At 274°C. this would induce a pressure variation of ±4 mm. The furnace temperature was recorded within ±0.1°C., corresponding to a pressure range of ±0.4 mm. The pressures could be read directly to ±1.0 mm. and were estimated with the aid of a magnifying lens to 0.1 mm. with a probable precision of ±0.3 mm.

The actual recorded fluctuation in pressures after equilibrium had been reached was ±1.0 mm., and this probably represents the over-all precision in the pressure values.

It is apparent that points that do not fall on the selected curve deviate by much more than the limits of experimental error. Table 3 shows the time that the sample was held at each new temperature. At each point, the changes in pressure stopped, except for small fluctuations caused by changes in barometric pressure, room temperature, and furnace temperature. After reaching an apparent equilibrium, the same temperature was maintained for one to five hours before going to the next temperature. Therefore, no entirely satisfactory explanation for the deviations can be given at this time.

The sluggishness of the reaction was even more pronounced for the Ames metal. A sample of chips prepared in the same manner as the Westinghouse sample showed no tendency to form the hydride until it was held at a hydride-forming temperature overnight. During this time, the reaction started extremely slowly, absorbing 3 ml. in 18 hours. After exposure to hydrogen for about two days at temperatures between 200°C. and 280°C., the rate increased

TABLE 3. DISSOCIATION PRESSURES OF "O_2" METAL HYDRIDES
(Westinghouse Metal)

Point Number	Temp., °C.	Dissociation Pressure, mm. Hg	Time to Reach Equilibrium (Hours)
1	387	1291	28
2	365	1170	21
3	325	778	3
4	294	365.5	19
5	274	215	42
6	201⁻	20.0	3
7	250⁻	88.7	18
8	234⁺	59.7	22
9	201⁻	19.8	21
10	336	659.6	25
11	361	859.5	21
12	368	982.6	17
13	255⁻	117.4	27
14	355	838.7	18
15*	303	300.7	19
16**	273	195.8	16

* Removed an additional 50 ml. H_2.

** Ames metal. This is the first point in a run now in progress.

slightly to about 1 ml. per hour at 280°C. Point No. 16 (Table 3, Figure 5) was obtained after 16 hours at this temperature.

Alloys of Tuballoy

Tuballoy-Columbium Alloys

Dilatometer Studies The dilatometer studies of Tu-Cb alloys containing up to 6% Cb have been completed and are summarized in Figure 6 in which the regions of alpha, beta, and gamma stability are outlined. The points plotted for each of the four compositions were selected from a number of dilatometer curves to give the best estimate of the boundaries. The results are very much like those obtained with the Tu-Mo alloys. The lower limit of the gamma field drops rapidly with increasing Cb content up to 4-5%. The beta field disappears at about 3%. The sluggishness of the alloys was quite evident from the long times that were required to complete the transformations within a reasonable range of temperatures.

Thermal Conductivity of 4% Cb Alloy The thermal conductivity of the 4% Cb tuballoy alloy in the as-received condition was determined in the range of 100 to 350°C. The as-received condition of this alloy appears to have been at least partially transformed to alpha, as indicated by the dilatometric studies. Also, this specimen and standard were only about half the diameter of the usual specimen, decreasing the accuracy of the determination, although the values are believed to be within 5%. While the nominal composition was 4%, analyses showed 3.66 and 3.88%.

The conductivity of this alloy lies between that of pure metal and the 5% Mo alloy. A graph of the data for the 4% Cb alloy and pure tuballoy is shown in Figure 1.

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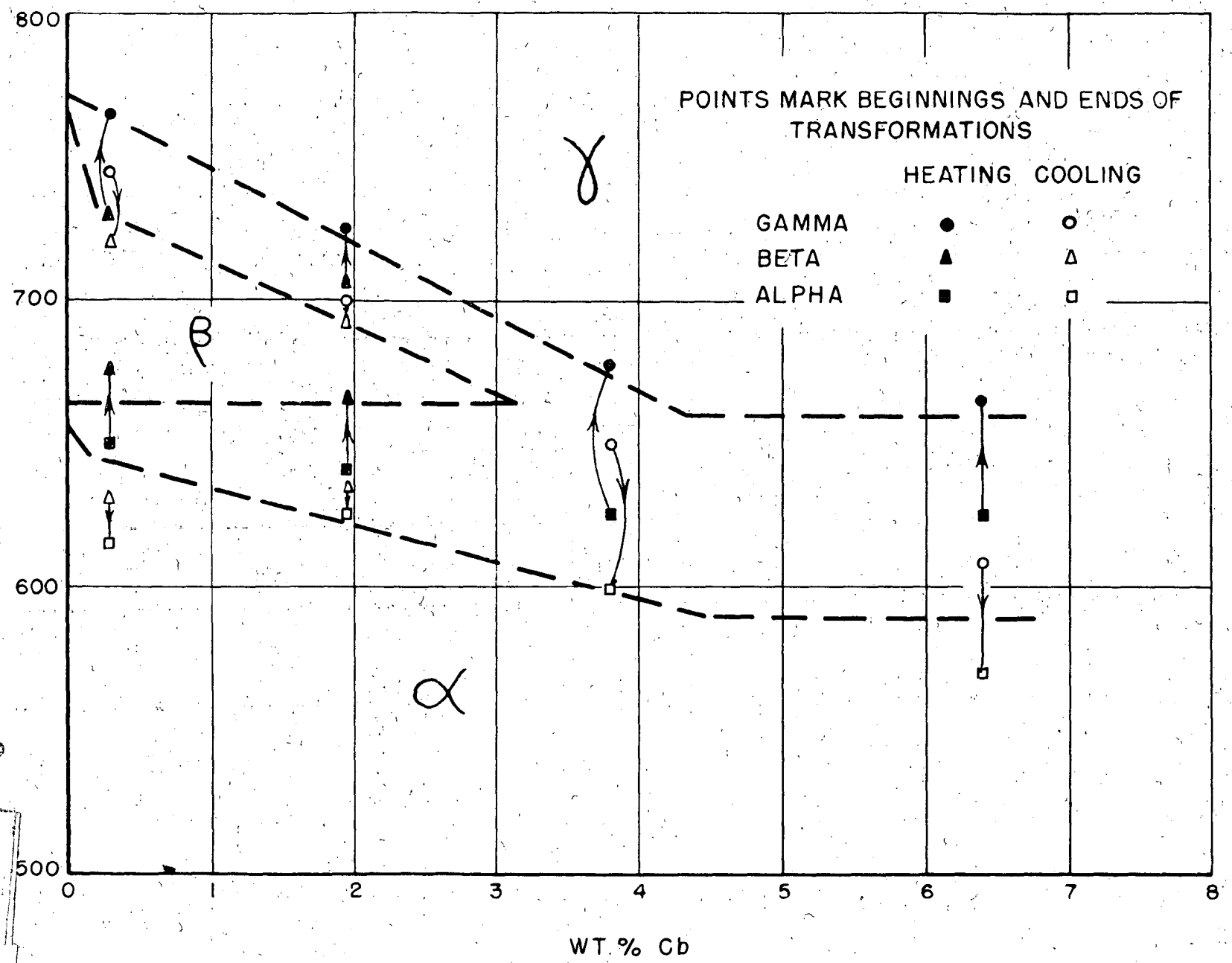

FIG. 6- SUMMARY OF PHASE CHANGES AS INDICATED BY DILATOMETER DATA ON Tu-Cb ALLOYS

Tuballoy-Titanium Alloys

Dilatometer Studies Three alloys in the low-Ti range were studied, but chemical analysis later showed that two of the specimens had practically the same Ti content. Consequently, the summary graph in Figure 7 contains only two compositions. The beta-gamma transformation is lowered somewhat by small amounts of titanium, but the alpha-beta transformation is not appreciably affected. The beta field persists to at least 2.3% Ti.

Corrosion Resistance The resistance of two titanium alloys to corrosion by boiling distilled water was tested. The samples were 0.375" diameter rods one inch long, having a nominal composition of 2.6% and 4% Ti. Later analysis, however showed them to be 2.27 and 2.30% Ti, respectively. A sample of unalloyed tuballoy was run at the same time for a standard.

The samples, with freshly abraded surfaces, were suspended in individual reflux condensers on glass tripods under the surface of the boiling water. At the end of 24, 72, and 96 hours, the samples were removed and all loose scale brushed off with a brush, wiped clean with a cloth, and weighed. The water was changed after each weighing. Total weight losses are shown in Figure 8.

The addition of 2.3% Ti reduced the weight loss to about one-fourth that of the pure metal. There were no noticeable differences in the corrosion products, and the attack was uniform over the entire surface. The rate of attack on all three alloys was constant over the period tested, showing no evidence of an initial induction period.

The weight loss of the 2.3% Ti alloy was consistently less than that of the 2.27% alloy. However, the difference was hardly enough to be significant.

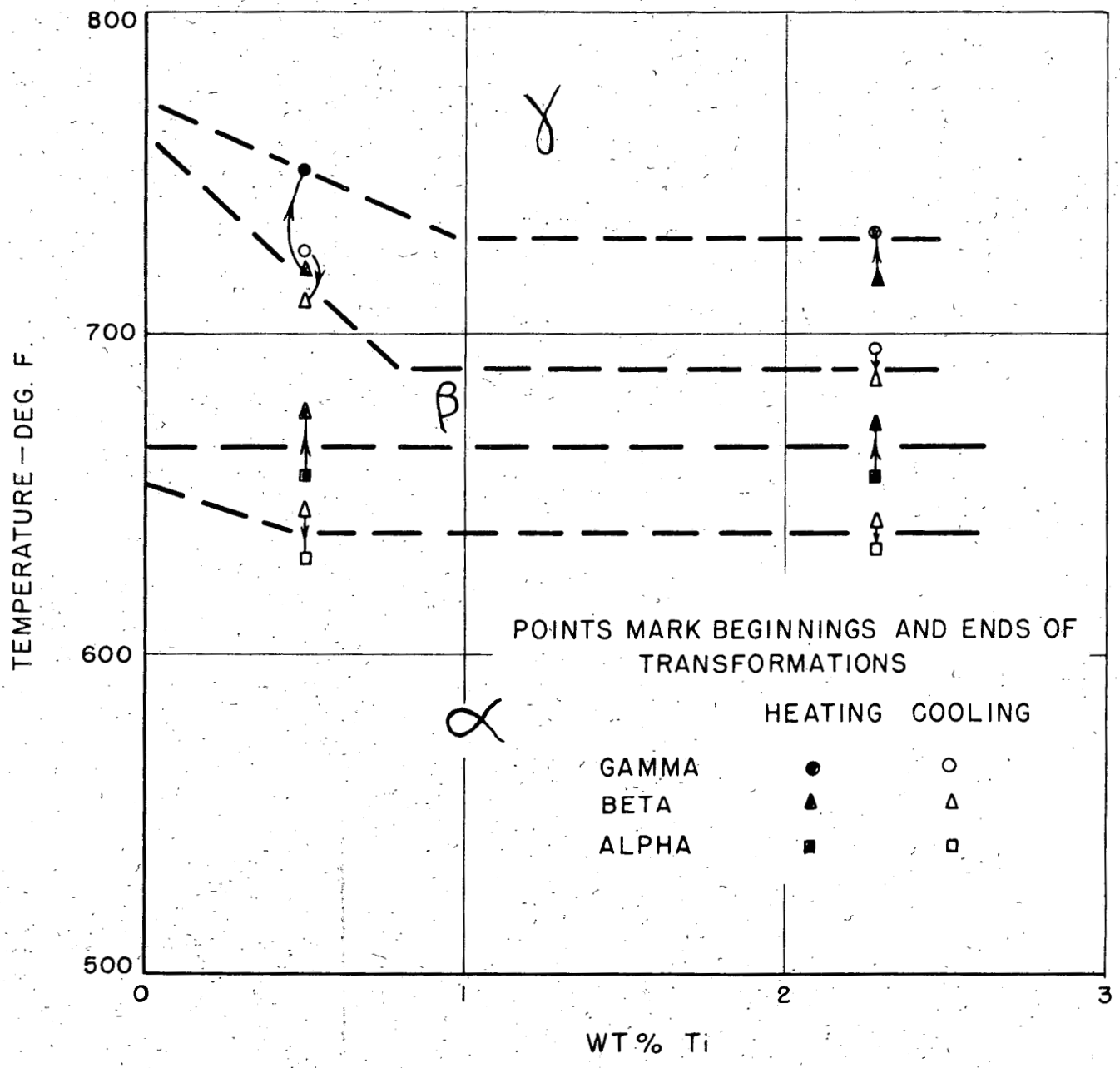

FIG 7 - SUMMARY OF PHASE CHANGES AS INDICATED BY DILATOMETER DATA ON Tu - Ti ALLOYS.

0-412

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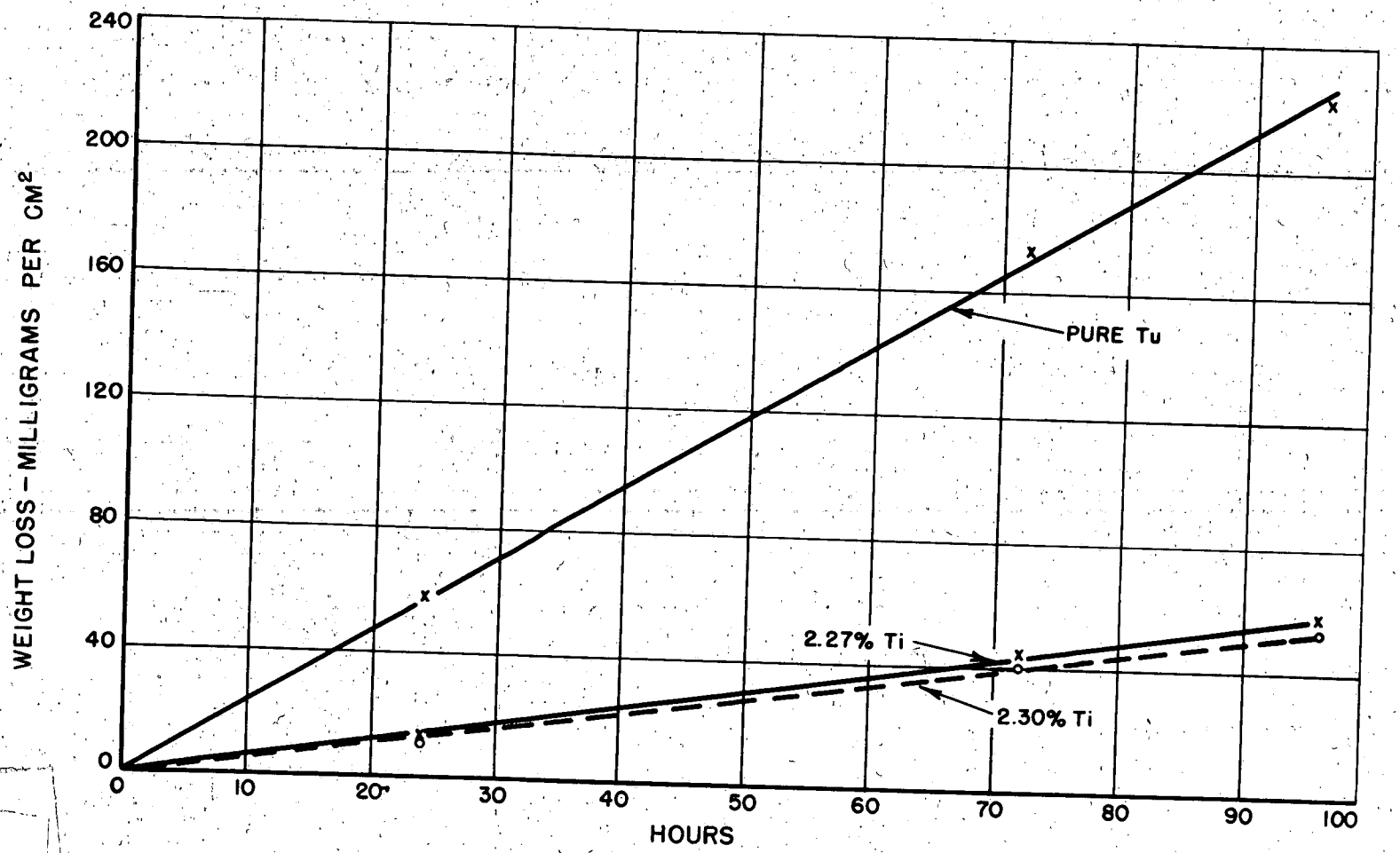


FIG 8 - CORROSION TESTS Ti-Tu ALLOYS IN BOILING DISTILLED WATER

34893

The effect of larger percentages of Ti is being investigated.

Alloys of Tuballoy and Indium

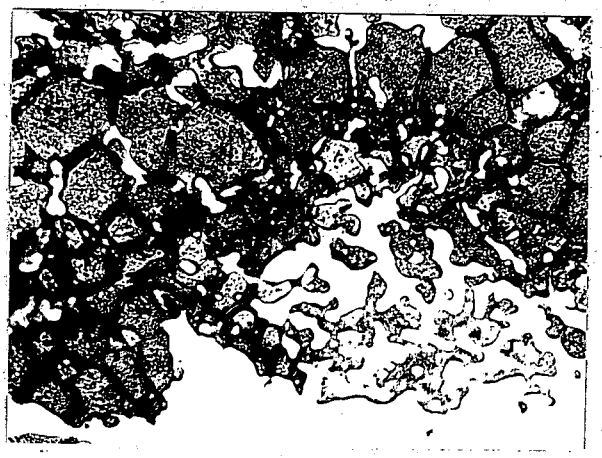
In continuing the investigation of various binary alloys of tuballoy, indium alloys of 5 and 10 weight per cent were made. The alloys were made in beryllia crucibles under a vacuum. Metallic indium was added to the molten base metal; then the melt was allowed to cool immediately.

As shown by the micrographs in Figure 9, the alloys obtained were not homogeneous. Both alloys showed a dark compound occurring in large patches in a two-phase matrix. The compound was moderately hard, but crumbled easily. So far, it has not been possible to homogenize the metal by heat treatment.

Tuballoy-Aluminum Alloys

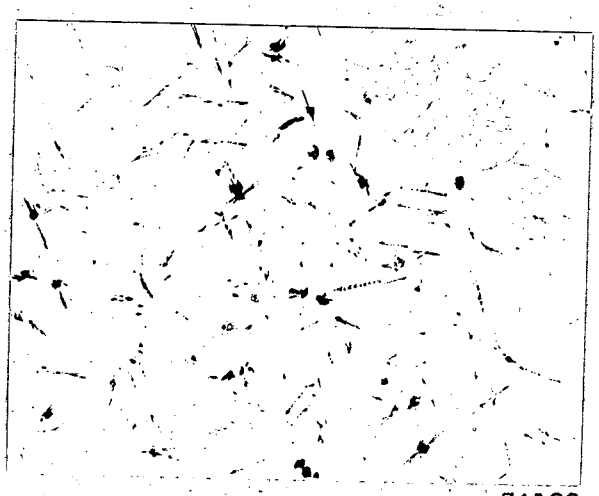
Fabrication Melts weighing 10 to 15 pounds were made in a clay-graphite crucible, using a gas-air furnace of aluminum with additions of tuballoy from 2 to 30%. For the lower alloys, the aluminum was allowed to reach about 1500°F. when the addition was made, stirring with a graphite rod. The melt was allowed to cool to 1300°F., or thereabouts, and poured into an iron ingot mold, giving an ingot approximately 6 x 10 x 1½". Pouring temperatures up to 1800°F. were required for the higher alloys, as shown in Table 4.

Structures of four of the cast alloys are shown in Figure 10. The 9% alloy consists of aluminum plus eutectic, while the 16.8% alloy is very close to the eutectic composition. The 18.11% alloy appears to be slightly hypereutectic, showing some primary compound and eutectic. These alloys close to the eutectic composition appear to have somewhat larger particles of compound with less lamellar structure than would be expected. The 29.1% alloy, of course, is strongly hypereutectic and shows massive needles of compound in a eutectic



34123

Compound.



34122

Matrix.

Figure 9. Structures obtained in the 10% indium alloys. Mechanical polish. Nitric-acetic etch. 250X.

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TABLE 4. MELTING AND ROLLING Tu-ALUMINUM ALLOYS

Intended Composition, % Tu	Analysis, % Tu	Pouring Temp., °F.	Hot Rolling, 800°F.	Cold Rolling	Remarks
2.25	1.88	1300	1.5 to .340", 12 passes, 2 reheats	.340 to .080", 4 passes, one anneal	
2.5	2.43	"	Ditto	Ditto	
3.0	3.10	"	"	"	
5.0	4.95	"	"	"	
8.0	7.0	"	1.5 to .340", 18 passes, 2 reheats	.340 to .080", 7 passes, one anneal	
10.0	9.0	"	Ditto	Ditto	
12.0	11.3	1320	1.5 to .147", 36 passes, 6 reheats	.147 to .080", 4 passes	
14.0	14.3	"	Ditto	Ditto	
16.0	16.3	"	"	"	
18.0	16.8	1330	"	"	Scalped at .63" to remove defects.
18.0 A	17.3	1380	1.3/1.5 to .200", 39 passes, 6 reheats	.200 to .080", 5 passes	All alloys, except 18%, showed cross checking and edge cracking during hot rolling and were scalped again at about 5/8" thickness, then rolled without further cross checking, but edge cracks formed up to 1/2" deep. The .200 to .080" reduction was started hot, but can probably be regarded as cold rolling as the stock would not hold heat long at this thickness.
B	18.1	"			
21.0 A	20.3	1450	Ditto	Ditto	
B	20.4	"			
24.0 A	21.2	1470	"	"	
B	23.8	"			
27.0 A	26.6	1720	"	"	
B	26.7	"			
30.0 A	27.3	1800	"	"	
B	29.1	"			

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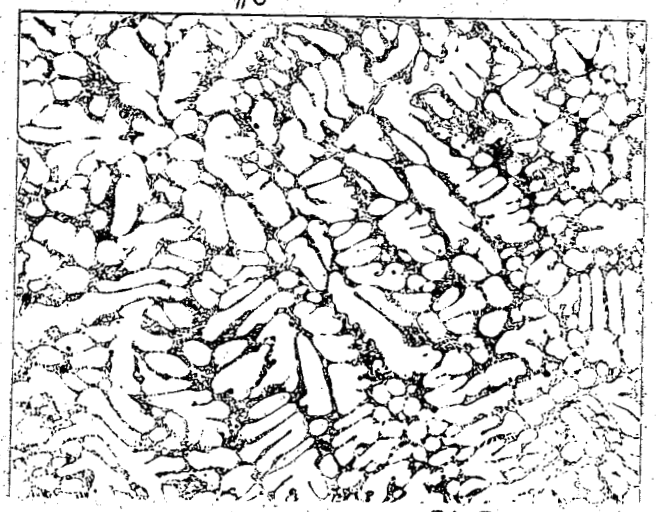
30

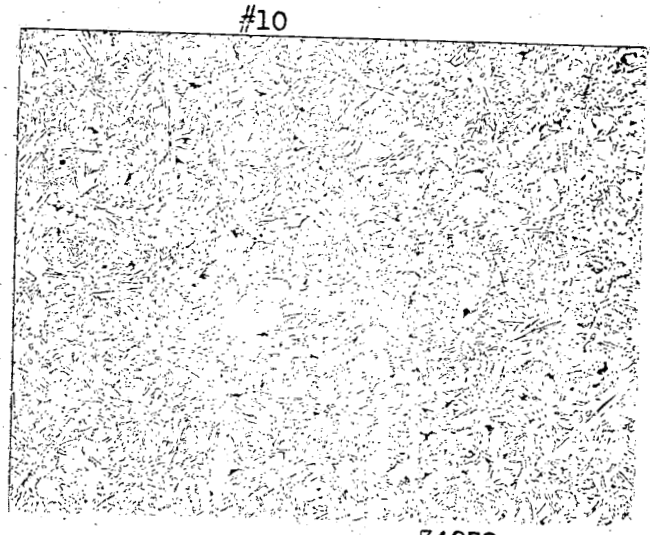
#6



34031

9.0% Tu.
Hypo-eutectic.

#10



34278

16.8% Tu.
Close to eutectic.

#11B

34548

18.1% Tu.
Slightly hyper-eutectic.

#15B

34556

29.1% Tu.
Hyper-eutectic.

Figure 10. Tu-aluminum alloys, Tu content as shown, cast structure.
NaOH etch. 100X.

633 032

matrix. Particles of a dark-etching phase will be observed. It is not clear that this is a different phase or some peculiarity of the etch used.

The ingots were radiographed and unsound portions near the top were removed. No serious segregation or unsoundness in the major part of the ingots was observed. The ingots were scalped and allowed to soak at 800°F. for two to four hours before hot rolling.

The data in Table 4 show some increase in the number of passes required for alloys containing 7 to 9% Tu. The 12 to 18% group rolled with considerably more difficulty than the alloys with lower Tu content, but it appears that these could be handled readily commercially.

The alloys containing 18 to 30% Tu were even more difficult to roll. The schedule used caused cross checking, which could probably be avoided by more frequent reheating and less reduction per pass. It is doubtful that these alloys would withstand more than 10 to 15% cold reduction. The 18% alloy was the only one of this group which did not cross check. Edge cracking was more serious with this group. These alloys could probably be produced in a commercial mill, but special rolling schedules would be required, losses would be considered excessive on the basis of present commercial operation, and, hence, their cost would be relatively high. The melting practice would require some adjustments, because of high pouring temperatures, which might be difficult with present mill equipment. It would appear from present information that an 18% alloy would be the highest content from a practical standpoint.

Preparation of Tu-Al Alloys With Oxide Additions It was desired to determine if suitable recovery could be obtained in making aluminum alloys by addition of tuballoy oxide. In order to obtain the most satisfactory recovery, it was considered desirable to make trials of adding the oxide directly to the

aluminum bath, to molten aluminum with a flux to insure contact between the aluminum and oxide (as well as remove any aluminum oxide formed) as briquettes of aluminum and oxide, and as an exothermic mix. The procedure and results are summarized in Table 5.

These results show 50 to 60% recovery of the tuballoy when using a cryolite slag. Direct addition to the metal gave negligible recovery of tuballoy, while the recovery in the exothermic mix tried was poor.

Properties of Tuballoy

Thermal Conductivity of Tuballoy

Data on the thermal conductivity of pure gamma-extruded tuballoy are shown in Figure 1 in comparison with the 4% Cb-tuballoy and thorium for the temperature range 100 to 350°C.

For the first attempt, a standard specimen was nickel-plated and the thermocouples resistance welded in place. The values obtained appear satisfactory, although some of the couples came loose through oxidation of the hot end of the specimen.

In order to check these results, arrangements were made to use a bare specimen, purging the air from the insulation with argon and allowing a small flow of argon to pass through the assembly during the determination. This arrangement gave values which showed less deviation than with the plated specimen, but plots of the two sets of data coincided exactly. The data obtained with argon protection are shown in Figure 1. The values for the 5% Mo alloy previously reported are 30 to 40% lower than those for the pure metal.

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TABLE 5. RECOVERY OF METAL WHEN ADDING Tu AS OXIDE

Method	Tu Charged, Per Cent	Tu Found, Per Cent	Tu Recovered, Per Cent	Total Metal Recovery, Per Cent
Addition of oxide to molten Al (1)	10	<0.1	< 1	83
Addition of oxide to molten Al	10	<0.1	< 1	77
Addition of oxide-cryolite mixture to molten Al (2)	10	6.7	61	91
Addition of oxide-cryolite mixture to molten Al	10	5.9	54	91
Aluminothermic reduction of oxide with exothermic mixture (3)	50	23	29	65
Aluminothermic reduction of oxide with exothermic mixture	50	23	29	65

(1) A five-pound melt of aluminum was heated to 1550°F. and oxide added with stirring. The melt was held five minutes at 1550 ± 25, cooled to 1375°F., skimmed, and poured.

(2) A five-pound melt of Al was protected with cryolite and heated to 2000°F. An oxide-cryolite mixture, containing sufficient cryolite to dissolve liberated Al_2O_3, was added with stirring. The melt was held 30 minutes at 2000°F., cooled to 1375°F., and poured.

(3) A mixture of oxide, 20-mesh Al, $NaNO_3$, Mg powder, CaO, and CaF_2 was added to a preheated crucible. The Al-tuballoy alloy separated as a button near the bottom of the crucible.

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Beta Phase of Tuballoy

Although it has not been possible to obtain the X-ray diffraction pattern of pure tuballoy in the beta phase, recent studies have shown that it is relatively easy to obtain the pattern of the beta phase in an alloy containing 0.6% Mo. Filings of this alloy were quenched from 690°C. and cleaned in nitric acid, which was removed by continuous dilution and decantation. A sharp diffraction pattern of a low-symmetry structure was obtained at room temperature with only very faint traces of oxide. Some of the same filings were resealed in an evacuated quartz tube and heated to 300°C. for 10 minutes. The resulting diffraction photogram, taken at room temperature, contained the same pattern plus a stronger pattern of the alpha phase. The same sample reheated to 600°C. for 10 minutes and cooled to room temperature gave only the pattern of alpha tuballoy. A second set of experiments was performed on another sample of the same alloy. A photogram taken at 690°C. contained the pattern of the same new phase. On cooling to room temperature in the camera -- a cooling rate which is very fast because of the small heat capacity of the furnace and very effective water cooling -- the same pattern was observed. At 600°C. the same specimen gave the pattern of the alpha phase. Again cooled to room temperature, the alpha phase was observed. Finally, the specimen was heated to 800°C., where the pattern of the gamma phase was obtained. Throughout this series, the pattern of oxide gradually became stronger, but never strong enough to obscure the phases of interest.

These two series of experiments seemed to require independent proof that the beta phase in 0.6% Mo-Tu can be retained at room temperature by quenching. This proof has been obtained by quenching dilatometer specimens from

690°C. and following the dilatation on subsequent heating in the dilatometer. In one case, during fairly rapid heating, the beta-to-alpha transformation started at about 120°C. and was completed in about 4 minutes at 200°C. Another specimen heated much more slowly started to transform at about 90°C., and the transformation was completed at 125°C. in 25 minutes. In both cases, the change in length was the same, within the limits of error, as was observed in normal alpha-beta transformation. It is believed that quenching stresses in the dilatometer specimens (1" long by 3/8" in diameter) may account for the transformation at lower temperatures than were observed in the filings used for X-ray work.

The diffraction pattern of beta retained at room temperature is given in Table 6. Preliminary examination suggests that the structure is orthorhombic.

Tuballoy-Nitrogen System

For the past 16 months, studies of the tuballoy-nitrogen system have been in progress whenever the apparatus has not been in use for more pressing phases of the project. At present, the apparatus is in use for studies with thorium, and it seems unlikely that more work will be done on the tuballoy-nitrogen system. For this reason, if not for the completeness of the results, the work is considered completed, and a summary report is being prepared. Some of the more important conclusions are summarized here.

In a closed system containing nitride plus nitrogen, the equilibrium pressure and temperature depend upon the composition of the nitride phase. The dependence upon composition is so critical that when equilibrium is reached at a given temperature and pressure, it is necessary to calculate the composition of the solid phase from the known mass of nitrogen in the gas phase. Conse-

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TABLE 6. X-RAY DIFFRACTION PATTERN OF 0.6% Mo-Tu ALLOY QUENCHED FROM 690°C. PHOTOGRAM TAKEN WITH CuKα AT ROOM TEMPERATURE

Spacings, A.	Relative Intensities	Spacings, A.	Relative Intensities
2.82	M	.966	F
2.57	VS	.948	M
2.48	S+	.934	F
2.42	S	.910	VF
2.33	VS	.899	VVF
2.28	MS	.867	VVF
2.15	M	.855	VVF
1.61	M	.846	M
1.52	MS	.828	F
1.50	M	.817	VF
1.45	MS	.803	F
1.41	M+	.792	MF
1.28	MF	.785	MF
1.25	VF		
1.24	MF+		
1.19	F		
1.17	F-		
1.16	VF		
1.06	VVF		
1.04	MF broad		
1.01	M		

quently, to obtain a straight line curve on a Log P vs. 1/T plot, it is necessary to hold the composition of the solid phase precisely constant by the addition or removal of nitrogen to produce pressure variations without changing the solid phase composition. If this is not done, the resulting equilibrium curve is not straight, but is convex upward. In the actual measurements, the composition of the solid phase was allowed to vary and was computed for each temperature and pressure to give a family of isotherms, showing the variation of composition as a function of pressure. From these curves, the equilibrium pressures and temperatures for the three compositions shown in Figure 11 were taken. From the slopes, the heat required to decompose the indicated formula weights to TuN were computed as follows:

$$TuN_{1.65} \longrightarrow TuN + 0.325\ N_2$$
$$\Delta H = 15{,}690 \text{ cal.}$$

$$TuN_{1.60} \longrightarrow TuN + 0.30\ N_2$$
$$\Delta H = 18{,}790 \text{ cal.}$$

$$TuN_{1.56} \longrightarrow TuN + 0.28\ N_2$$
$$\Delta H = 19{,}550 \text{ cal.}$$

By extrapolation, the value

$$TuN_{1.50} \longrightarrow TuN + 0.25\ N_2$$
$$\Delta H = 21{,}900 \text{ cal.}$$

is obtained, which gives the value

$$\Delta H = 43{,}800 \text{ cal./mol}$$

for the heat of decomposition in the reaction

$$Tu_2N_3 \longrightarrow 2\ TuN + 0.5\ N_2$$

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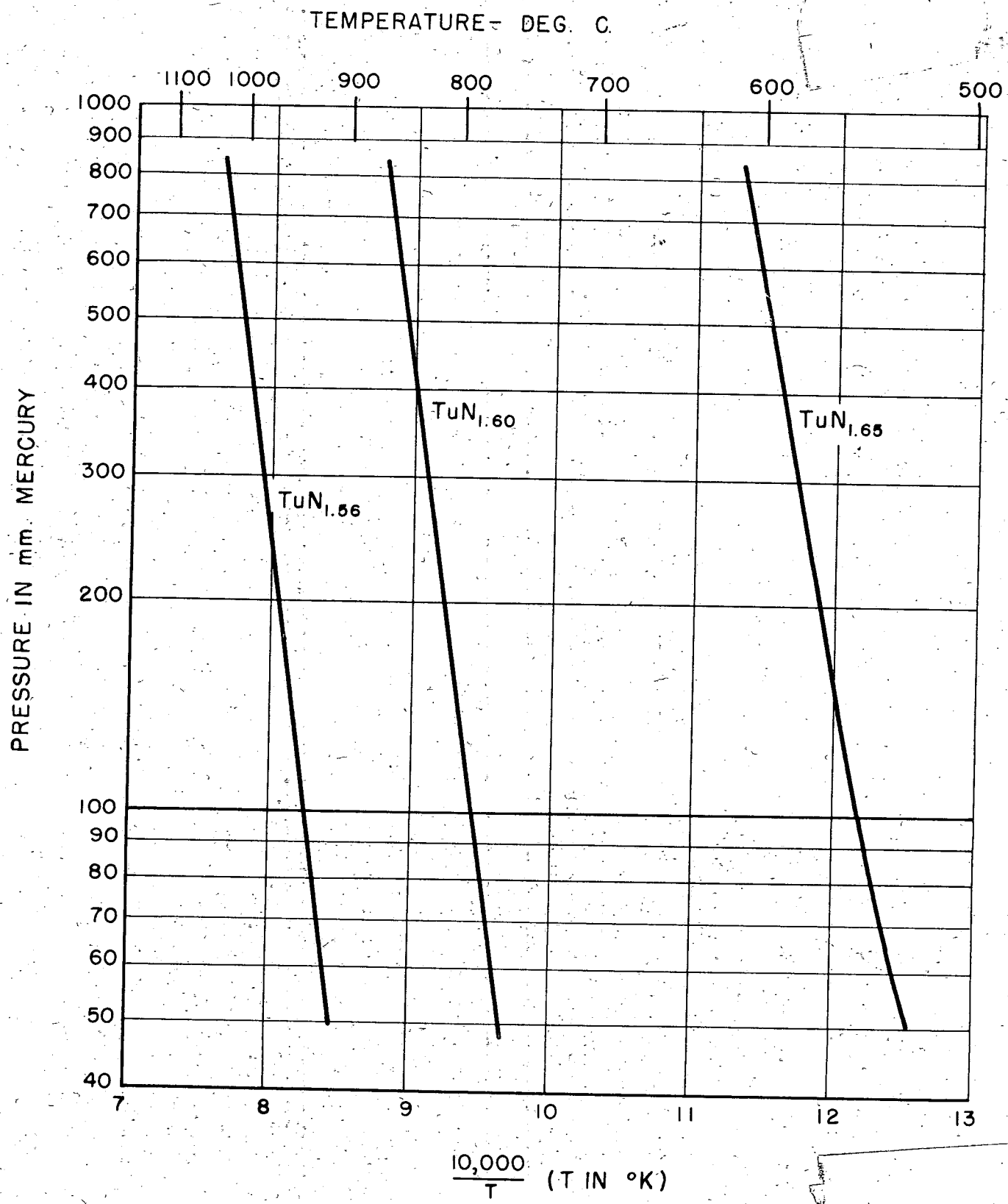

FIG. 11- NITROGEN PRESSURE IN EQUILIBRIUM WITH THREE DIFFERENT COMPOSITIONS OF TUBALLOY NITRIDE AT VARIOUS TEMPERATURES

633 ~ 040

The highest composition obtained in this work was $TuN_{1.68}$ at 492°C. and 825 mm. pressure. At 1048°C. and 50 mm. pressure, the composition was $TuN_{1.52}$. Over this range of temperatures and pressures, the equilibria were completely reversible.

The lower nitride has not been studied because of its high stability at readily attainable temperatures. The following experiment is typical of several that demonstrate this stability: A sample known to have the composition $TuN_{1.637}$ was pumped out with an automatic Toepler pump connected to the specimen chamber. Evolution of nitrogen was slow up to 1000°C. At 1135°C. rapid evolution started and continued until practically all of the extractable nitrogen was removed. Continued pumping for an hour at 1200°C. removed very small amounts of gas. From the measured gas removed by the Toepler pump, the final composition was computed to be $TuN_{0.96}$. From this experiment and others, it is estimated that the nitrogen pressure in equilibrium with TuN at 1200°C. is less than one micron.

X-ray diffraction examination of compositions near TuN indicate that this compound has a face-centered cubic lattice with a_o=4.88 A. The higher nitrides formed in equilibrium with nitrogen at temperatures between 800°C. and 1050°C. consisted of a body-centered cubic lattice, a_o=10.68 A. At lower temperatures, diffuse patterns corresponding to face-centered cubic lattices with a_o=5.29 to 5.31 A. were observed. It is possible that the true lattice parameter for these structures is twice the apparent value, and that the structures are actually identical with body-centered cubic, high-temperature form.

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FUTURE WORK

Further studies of the properties of thorium are in progress.

The addition of tuballoy oxide to aluminum to produce alloys is being studied.

The solubility limit of tuballoy in aluminum is being investigated, as well as physical properties of these alloys. Experiments are also in progress on Alcladding the tuballoy-aluminum alloys.

Studies of the high-temperature phases of tuballoy by means of X rays is continuing.

Preparation of centrifugally cast beryllium tubes is under way.

HWR:HRN:LHG:KRJ:HAS:IC:MWM:CJS/LM
February 10, 1945