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PROGRESS REPORT

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on

METALLURGY OF TUBALLOY

to

UNIVERSITY OF CHICAGO

from

BATTELLE MEMORIAL INSTITUTE

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SUMMARY

Further X-ray and dilatometer studies of Tu-Mo alloys containing under 5% Mo have confirmed the regions of alpha, beta, and gamma stability given in the last report.

The thermal conductivity of 5% Mo-Tu has been determined as follows:

Heat Treatment	Thermal Conductivity, watts/cm./°C.	
	at 150°C.	at 300°C.
As received or quenched from 700°C.	0.17	0.22
Annealed 40 hours at 520°C.	0.21	0.245

The hydrogen solubility in 5% Mo-Tu is about 5.3 p.p.m. at 500°C. and 11.4 p.p.m. at 750°C. The solubility increases with increasing temperature in both the alpha and gamma regions.

The 5% Mo alloy heat treated to the gamma condition shows a tensile strength of 80-85,000 p.s.i. with practically no ductility. The fractures showed tarnishing of the rim, but remained bright in the center, indicating possible transformation to alpha caused by stress. Specimens treated at

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500°C. to a structure substantially alpha with some gamma gave a tensile strength of over 180,000 p.s.i. with a yield of over 150,000 p.s.i. While the strength at 600°C. was approximately the same as for pure metal, the strength at 520°C. was 4-5 times that at 600°C.

Hot-hardness tests showed considerably higher values in the alpha region than pure metal, but hardness values in the gamma region agreed well with those for gamma pure metal. No indication of the hard beta phase was noted.

Annealing tests on cold-rolled 5% Mo strip showed an increase in hardness up to 400°C. There was then a gradual decrease in hardness until 650°C., when the hardness dropped sharply to about 58 R_g and remained substantially the same up to 750°C.

Further tests on diffusing of sprayed Mo coatings and production of a coating by reduction of molybdenum-black coatings do not appear promising.

Dilatometer and X-ray studies show that alloys of Tu containing up to 6% Cb are very similar to Tu-Mo alloys as regards solid-state transformation. The region of beta stability is very small and disappears between 2 and 4% Cb.

Rough, exploratory experiments on Westinghouse thorium indicate that temperatures of 600°C. or higher are required for satisfactory annealing of cold-worked thorium. With the single small sample tested, a reduction in thickness of 60% by cold rolling with no intermediate anneals gave a hardness of Rockwell E 83. Fifteen-minute anneals at successively higher temperatures produced no appreciable softening until 600°C. was reached, which lowered the hardness to about E 68.

Extruded rods of Ames and Westinghouse thorium have significantly different electrical resistivities, viz., Ames, 28.7 microhm cm.; Westinghouse, 20.4 microhm cm. at 26°C.

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Ten small vacuum melts of alloys with indium, columbium, germanium, and titanium were prepared for study.

EXPERIMENTAL DATA

Tuballoy-Molybdenum System

Dilatometer and X-Ray Studies

Further studies of tuballoy containing less than 5% Mo have confirmed the regions of alpha, beta, and gamma stability summarized in Figure 142 of the last report. The stable beta region continues to appear small, and there seems to be no beta phase in alloys containing more than about 2% Mo. Attempts to determine the structure of the beta phase continue to meet with failure.

The face-centered-cubic structure with lattice parameter of about 4.93 Å, which has been discussed in the last two reports, has been given further study. All the data are compatible with the interpretation that this phase is an oxide of tuballoy, probably the monoxide recently studied at Ames. It is interesting to note, however, that the pattern of this phase is very faint in diffraction patterns made at high temperatures when the quartz sample tube has been evacuated with a mechanical vacuum pump. When a mercury diffusion pump is used, the face-centered-cubic pattern is much stronger. The change from mechanical pump to diffusion pump evacuation of specimen tubes some two months ago coincides with the appearance of strong patterns of this phase.

Thermal Conductivity of 5% Mo-Tuballoy

The thermal conductivity* of a sample of 5% Mo alloy has been determined for the range 100° to 350°C. with the sample in three heat-treated states, viz, (1) as-received, (2) after annealing for 40 hours at 520°C., and (3) after water-quenching from 700°C. From studies of other samples of the same alloy, it was believed that this sample was in the metastable gamma state as received. The 520°C. anneal was intended to produce all alpha, and the quench was intended to retain the gamma.

Results are given in Figure 152. The conductivity in the alpha state is definitely higher than in the metastable gamma state. In both cases, the conductivity increases with increasing temperature, but the temperature coefficient is greater for the gamma state. Measurements on pure tuballoy are to be made for comparison with these results.

Hydrogen Solubility in 5% Mo-Tuballoy

One run was made using a massive sample approximately 5/8" long with a 1/2" diameter. The apparatus was similar to that used in previous gas solubility studies. Much hydrogen was lost by diffusion through the fused silica tubing before equilibria were attained at temperatures above 550°C. After applying rather large corrections for diffusion losses, the solubility figures obtained were of the same magnitude as those found in the second run.

In order to shorten the time required to reach equilibrium, the specimen used in the second run was made up of 19 strips of metal approximately 1/16" x 3/32" x 1" long. A new specimen tube was designed for the purpose of minimizing diffusion losses (Figure 153). It consisted of a double-walled chamber of clear, fused silica. The specimen was loaded through the small-

* The apparatus and method were similar to those described in Bur. Stand. J. Res. vol. 12, pp. 429-440, 1934.

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FIGURE 152 — THERMAL CONDUCTIVITY OF 5% Mo-TUBALLOY.

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bore silica tubing, and a final seal was made at a point about 15" from the bulb containing the metal. Thus, contamination of the specimen was avoided.

The outer chamber was filled with hydrogen which was maintained at approximately the same pressure as the hydrogen in the inner (specimen) chamber. The buffer chamber extended about four inches out of the furnace so that all parts of the system at elevated temperatures were protected.

In obtaining the first series of points (Nos. 1-13 in Figure 154), nothing out of the way was noticed until Point No. 5 at 857°C. was attempted. After three hours, H₂ was still being sorbed. Points No. 6 and No. 7 indicate a line of the same slope as obtained from Points No. 3 and No. 4, but 1.1 p.p.m. higher. Again the temperature was raised (to 944°C.) and sorption appeared to be continuing after 19 hours. After dropping to 857°C. (Point No. 10), no change occurred in 90 minutes, so Points No. 11 and No. 12 were taken, and a new "solubility" line, now 2.2 p.p.m. above the original line, was obtained.

It appears that a permanent loss or sorption of H₂ occurred at temperatures above 850°C. The loss was not a function of time, since similar losses occurred in three hours at 857°C. and again in 19 hours at 944°C. The loss was probably not due to diffusion from the system because the apparatus, as described above, provides no diffusion gradient and also because the losses were independent of time. However, it is apparent that a certain amount of hydrogen is lost or tied up irreversibly. This was proved by taking Point No. 13 and then pumping out and analyzing the gas in the system. The volume of gas obtained (100% H₂) represented all that could be obtained in four days at 700°C. with the pressure less than 100 microns Hg.

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FIGURE 154—HYDROGEN SOLUBILITY IN 5% Mo-Tu IN EQUILIBRIUM WITH HYDROGEN AT 750mm. PRESSURE. THE EQUILIBRIUM POINTS WERE TAKEN IN THE ORDER INDICATED BY THE NUMBERS. FOR THE REASONS GIVEN IN THE TEXT, THE REVERSIBLE SOLUBILITY IS BELIEVED TO LIE CLOSE TO THE SOLID CURVE.

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Recalculating Point No. 13 using the volume of H_2 extracted, Point No. 13' was obtained, which fell close to the original line and verified the fact that some permanent loss or combination of H_2 had occurred.

After this outgassing, H_2 again was admitted to the system and Points No. 1A through No. 6A were taken. To avoid unnecessary H_2 loss, the system was held at $946^\circ C$. (Point No. 2A) for only 45 minutes, during which time no noticeable change in volume occurred. The point appears somewhat high, but the following Points No. 3A and 4A fall on the previously determined line. At $447^\circ C$. (Point No. 5A), continuous slow sorption took place. Upon raising the temperature to $519^\circ C$., some recovery toward the solubility curve occurred. It appears that a reaction, possibly hydride formation, is beginning to occur at $447^\circ C$., although the pressure-temperature curve for the decomposition of the hydride in equilibrium with pure tuballoy and hydrogen indicates that no hydride should form at this temperature and pressure ($447^\circ C$., 747 mm.).

The true reversible solubility at 750 mm. pressure is believed to be close to the solid curve in Figure 154. As already pointed out, the points above the curve represent nonreversible sorption or loss of hydrogen which has not been explained. Comparison with previous data (Figure 1, report of February 10, 1944) shows that the hydrogen solubility in the high alpha region is approximately $2\frac{1}{2}$ times greater than in pure tuballoy. In the gamma region, however, the solubility in the 5% Mo alloy is somewhat lower than in pure tuballoy.

Mechanical Properties of 5% Mo Alloy

Rods $7/8"$ and $1/2"$ in diameter were prepared by rolling at $1400^\circ F$. standard slugs of the 5% Mo for various tests. Sections were heat treated as described below.

959-1A

Room-Temperature Tensile Tests Two blanks were quenched after heating at 700°C. for one hour and one after heating at 500°C. for one hour. These were then machined to standard .505" test specimens. The specimens were designated 700-1, 700-2, and 500, corresponding to the temperature of heat treatment.

Loading and unloading tests, first to 10,000 p.s.i. and then to 25,000 p.s.i., were made on the 700°C. treated or gamma specimens, using two Tuckerman extensometers and a lateral strain gauge consisting of two SR4 electric strain gauges on a steel ring, as previously used on pure metal specimens. Examples of these loading and unloading curves for both lateral and longitudinal strain are shown in Figure 155. The 500, or alpha, specimen was similarly loaded, but using only the Peters extensometer, as it was considered that its behavior would be similar to pure metal, on which data had previously been reported. Following the loading and unloading tests, the specimens were broken, giving curves as shown in Figure 156. These curves show a substantial straight portion as compared to pure metal curves.

The results of these tests are summarized in Table 37. It will be noted that the properties of the gamma specimens are not greatly different than those previously reported for gamma-extruded material. The elongation values for this heat treatment are indeterminate on account of small fractures throughout the gauge length. There appears to be a considerable hardening effect in heating for one hour at 500°C., which is known to give incomplete transformation. Whether this is an effect of aging or merely the distribution of the alpha and gamma phases is not clear. The strength and yield properties in this condition are much higher than any reported for pure metal.

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FIGURE 155
ELASTIC DEFORMATION OF SPECIMEN 700-1. CURVES FROM ONE
TUCKERMAN EXTENSOMETER AND LATERAL STRAIN GAGE.
5% Mo-Tu

FIGURE 156
ROOM TEMPERATURE STRESS STRAIN CURVES MADE WITH PETERS EXTENSOMETER.
5% Mo-Tu

33999

TABLE 37. MECHANICAL PROPERTIES OF 5% Mo ALLOY

Heat-treating temperature	500°C.	700°C. (1)	700°C. (2)
Ultimate strength, p.s.i.	183,000	80,000	83,500
Y. S., p.s.i., 1% offset	153,500	51,250	52,050
Y. S., p.s.i., 2% offset	166,500	58,750	59,050
Elongation in 2"	6%	1% (?)	1% (?)
Reduction of area	8%	0	0
Brinell hardness in grip	363	160	163
Type of fracture	fine, flat	fine, rough edge	fine, rough edge
Character of curve	smooth	smooth	smooth

Figure 157 shows the fractures of these specimens after some time at room temperature. The center portions of those with the gamma heat treatment remained bright, suggesting that the surface layers may have transformed to alpha through stress either from machining or testing, since the specimen heat treated at 500°C. tarnished throughout.

Elastic Constants Table 38 summarizes the values obtained for the modulus of elasticity and Poisson's ratio. The values for the gamma state compare reasonably well for those reported for pure metal.

A value for the elastic modulus of the specimen treated at 500°C. was calculated, giving 38.5×10^6 and Poisson's ratio at .50. This value is much higher than any previously reported and may reflect inaccuracies with the extensometer used. However, the results with this extensometer on the gamma specimens checked well with those from the Tuckerman gauges. Further tests seem indicated. It is interesting to note that when the values for the elastic modulus of pure metal, in Report No. 13, are extrapolated to no load a value of about 35×10^6 is obtained.

High-Temperature Tensile Tests Elevated temperature tests were made on standard 1/4" test specimens in an argon atmosphere at 520°C. and 600°C. on stock from the 1/2" diameter hot-rolled bar. Both specimens were held at temperature about 2 1/2 hours before testing. The appearance of the specimens after testing is shown in Figure 158, the 600°C. specimen showing almost 100% reduction in area.

The results are shown in Table 39. The strength values at 600°C. are slightly higher than those obtained on rolled pure metal at the same temperature, but the ductility is very much greater (see B.M.I. Report No. 2, pp. 57). The properties at 520°C. are very much higher than for pure metal at 600°C.

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Figure 157. Appearance of fractures of room-temperature tensile specimens after tarnishing. Temperature of heat treatment is indicated in figure.

600°C.

520°C.

959-16

33984

Figure 158. Appearance of elevated-temperature test specimens after test.

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TABLE 38. ELASTIC CONSTANTS OF 5% Mo-Tu

Values are average of all runs in which Tuckerman gages are used.										
Load, p.s.i.	Increasing Load				Decreasing Load				Average	
	700-1		700-2		700-1		700-2		Mod.	Poisson's
	Modulus Elasticity	Poisson's Ratio	Modulus Elasticity	Poisson's Ratio	Modulus Elasticity	Poisson's Ratio	Modulus Elasticity	Poisson's Ratio		
5000	16.3	.40	17.4	.38	16.5	.40	18.0	.36	17.0	.39
10000	16.3	.40	17.5	.39	16.5	.40	16.9	.37	16.8	.39
15000	16.8	.38	15.9	.41	18.1	.37	17.7	.36	16.8	.38
20000	16.9	.38	15.9	.41	18.1	.37	17.7	.36	16.8	.38
All loads	--	--	--	--	--	--	--	--	16.9	.38

Note: In modulus values, $\times 10^6$ has been omitted.

95-9-17

TABLE 39. ELEVATED-TEMPERATURE TENSILE RESULTS FOR 5% Mo-Tu

Test Temp., °C.	Ultimate Tensile Strength	Yield Strength, p.s.i., 1% Offset	Yield Strength, p.s.i., 2% Offset	Elongation, Per Cent	Reduction of Area
600	14,200	8,400	8,870	273	99.1
520	64,000	24,200	26,800	48	73.1

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Hot-Hardness Tests Hot hardness of the 5% Mo alloy was determined by the mutual indentation method previously described. These results are given in Table 40, including the room-temperature value on the as-rolled 1/2" rod determined by standard Brinell. The specimens used in the high-temperature tests were machined from the hot-rolled 1/2" bar used for the high-temperature tensile tests and were tested without further heat treatment.

The values vary considerably from those reported for pure metal (B.M.I. Report No. 5, p. 169, CT-688). The hardness is substantially higher in the alpha temperature ranges; no indication of the hard beta phase is noted, but the hardness of gamma metal compares favorably. These tests are in agreement with the elevated-temperature tensile tests.

Annealing of 5% Mo-Tu alloy

Samples of 5% Mo-Tu were given annealing treatments after cold rolling to determine the effect of annealing temperature upon hardness and structure.

The material used was quench-annealed at 700°C., then cold-rolled with a 60% reduction. The cold-rolled material was then annealed one-half hour at temperatures up to 750°C. before hardness readings were made and the structures examined. The samples were heated in argon and water-quenched.

Again Rockwell G readings were used. This scale was not quite adequate, for hardnesses above 100 were encountered. It was used to facilitate comparison with previous work. The results of the hardness tests are shown in Figure 159.

There was a marked increase in hardness up to 400°C. At 500°C. a gradual softening began. This continued to 600°C. There was a great loss of hardness at 650°C. Subsequent heating did not cause any marked change in hardness.

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TABLE 40. ELEVATED-TEMPERATURE HARDNESS OF 5% Mo-Tu

Testing Temperature, °C.	Brinell Hardness	Load, Kg.	Remarks
Room	195	3000	standard ball
400	253	2000	
500	133	2000	
520	141	2000	at temperature 45 min.
600	69	500	
650	23	500	2000 kg. flattens
750	14	500	
800	12.6	500	at temperature 45 min.
900	0	500	flattened

Note: All specimens were held at temperature 30 minutes, except as noted.

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FIGURE 159—EFFECT OF ANNEALING $\frac{1}{2}$ HR. AT TEMPERATURE ON HARDNESS OF 5% Mo-Ti.

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The samples were polished mechanically and etched with a mixture of nitric and acetic acids. This method has been used previously for Mo-Tu alloys. The samples heated from 500°C. to 600°C. showed a fine lamellar structure. This disappeared completely in those heated above 650°C.

It would appear that a complete anneal can be obtained by heating above 650°C. Further work, using different etches, will be done to determine more completely the structures obtained.

Molybdenum Coatings

Sprayed Molybdenum Coatings The diffusion of sprayed molybdenum coatings was studied further in an effort to improve the diffusion characteristics of such a coating. As previously reported, the diffusion of the sprayed coating into the base metal was spotty, even after 10 hours at 1100-1125°C. and appeared to be dependent on the bond obtained during spraying. Efforts to improve this bond by altering surface preparation and spraying conditions were unsuccessful. In view of the high temperature required and the lack of uniform diffusion, this method of coating does not appear to be promising.

Reduced Molybdenum-Black Coatings Some additional work has been done on the reduction of Mo-black coatings. Electrolytically applied molybdenum oxide, when reduced in hydrogen, was nonadherent and was separated from the base by a nonmetallic layer. In order to improve the wetting action of the reduced Mo, the possibility of using Ni as a carrier or binder was investigated. Using a process similar to the duPont Mo-Black Process, coatings containing approximately 10% Ni, 45% Mo, and the remainder oxygen were applied to the surface of tuballoy samples. These coatings were then reduced by heating in hydrogen.

The reduced coating consisted of a loose metallic powder under which was a bright gray surface. The microstructure of this adherent coating was similar to that obtained by cementation in Mo powder, but was more uniformly distributed. The effect of the temperature and time of the reduction were varied without improving the resulting coating.

A corrosion test on a coated sample showed it to be more resistant to water vapor than the pure metal. However, there appeared to be uncoated spots from which corrosion proceeded.

Nickel-plated tuballoy samples were also coated with this Mo-black and reduced, but the reduced coating was not adherent, even though temperatures as high as 900°C. were tried.

Tuballoy-Columbium System

Dilatometer Studies

A study of the transformations in alloys with nominal Cb contents of 0.75%, 2%, 4%, and 6% has been made. Because the work is still in progress and because chemical analyses of the Cb contents are not yet available, curves and data summarizing the transformation temperatures will be presented in a later report. It may be said, however, that the Cb alloys are nearly identical, as regards solid-state transformations, with the Mo alloys. The diagram for the Mo alloys, Figure 142 in the last report, summarizes almost equally well the tentative data for the Cb alloys. The principal difference seems to be that Cb does not lower the transformation temperatures quite so much as Mo. With 4% Cb the lower limit of the gamma region appears to be about 680°C., nearly 50°C. higher than for the same weight or atomic per cent of Mo.

95-9-23

X-Ray Studies

Nominal 6% Cb alloy quenched from 700°C. retained the gamma structure with no trace of alpha. The lattice constant of the gamma at room temperature was about 3.52A as compared with the quenched 5% Mo value of 3.43A. The larger radius of the Cb atom may account for this difference.

Hot-camera and quenching studies on other compositions are in progress.

ThoriumPreliminary Annealing Experiments

A small cylinder of Westinghouse thorium in the sintered state was used for a rough survey of annealing temperatures. The piece, originally measuring approximately 1/2" long by 7/16" in diameter, was heated in a gas flame and hammered into a rectangular shape. After very brief annealing at a red heat in the gas flame, the hardness fell in the range 80-87 Rockwell E. The sample was then given three successive cold reductions of 15 to 20% in a small rolling mill with brief intermediate anneals in the gas flame. Cold-rolling reductions of 15 to 20% generally raised the hardness to Rockwell E 91-95, and brief (not over 1 min.) anneals at bright red heat (900 to 1000°C.) lowered the hardness to E 80-85. After the third rolling (from .110" to .093"), a half-hour furnace anneal in argon at 815°C. lowered the hardness from 92 R_e to 74 R_e, and a second half hour at 1100°C. further lowered it to 69 R_e. The piece was then cold rolled from .093" to .038", a 60% reduction that raised the hardness to an average E 83. Successive

15-minute anneals gave the following results:

Annealing Temperature, °C.	Hardness Readings, Rockwell E*		
	Number of Readings	Average	Range
400	6	85	80-92
500	5	88	79-92
600	5	68	63-73
700	7	75	61-81
800	6	70	59-78
900	9	67	58-75

* 1/8" ball, 100 kg. load

In view of the wide scatter in individual hardness measurements which may be attributed in part, at least, to the specimen being too thin for this type of hardness measurement, the only conclusion that can be drawn is that temperatures of about 600°C. are required for satisfactory annealing of Westinghouse thorium.

Electrical Resistivity

The electrical resistivities of three extruded rods, 6" x 0.492", have been measured at 26°C. on a Kelvin double bridge. The results were as follows:

Sample	Microhm cm.
Westinghouse, ends numbered 5 and 6	20.4
Ames, ends numbered 3 and 4	28.7
Ames, ends numbered 5 and 6	28.8

The Ames thorium is significantly higher in resistivity. This is a definite indication that the impurities in the metal from the two sources

are different even though the Ames metal may not necessarily contain more impurities.

Alloy Preparation

Small vacuum melts of 5 and 10% indium alloys, an additional amount of 10% Ge alloy, .75 and 1.5% Cb alloys, and .5, 1.0, 1.5, 2.6, and 4% Ti alloys have been prepared. The Cb alloys are to be used for dilatometer studies. No tests have been conducted on any of these alloys.

FUTURE WORK

Fabrication of aluminum with various amounts of tuballoy added is being studied.

The properties of the Mo, Cb, and Ti alloys are being studied. This includes thermal conductivity, metallography, X-ray and dilatometer studies, and determination of physical properties.

A small amount of thorium has been received for investigation of properties including methods of working, gas solubility, hydride formation, etc.

HWR:HRN:LHG:JRK:HAS:MWM:MH:OL/LM
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