

QUARTERLY PROGRESS REPORT
A STUDY OF TUNGSTEN-TECHNETIUM ALLOYS
OCTOBER 1, 1964-JANUARY 1, 1965

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QUARTERLY PROGRESS REPORT
A STUDY OF TUNGSTEN-TECHNETIUM ALLOYS
OCTOBER 1, 1964-JANUARY 1, 1965

By

The Staff of Metallurgy Development Operation
Hanford Laboratories

January 1, 1965

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INTRODUCTION

Technetium is a sister element to rhenium and has many properties that are similar to rhenium. It is predicted that technetium will have about the same effects on tungsten as rhenium in regard to increase in workability, lowered ductile to brittle transition temperature, and improved ductility.

The objectives of the current work are to recover technetium from fission product wastes at Hanford Atomic Products Operation and reduce to purified metal; prepare W-Tc alloys containing up to 50 at.% Tc; fabricate the alloy ingots to sheet stock, assessing the effect of technetium on workability; and perform metallurgical and mechanical property evaluation of the fabricated alloys.

Previous reports in this series have described the separation and purification of 800 g of technetium metal powder and initial melting and fabrication attempts with pure technetium metal.

CURRENT PROGRESS

During the past quarter tungsten and technetium powders were weighed, blended, and pressed isostatically in a rubber mold to form compacts for arc melting. Eighteen 35 g compacts were made with two compacts of each of the following compositions: tungsten, and W-2.5, 5, 10, 20, 30, 40, 50, and 60 at.% Tc. Tungsten powder with an average particle diameter of 0.71μ obtained from General Electric Company, Cleveland, Ohio was used in this work. The analysis of this material is given in Table I.

* Previous Reports: HW-83550, Quarterly Progress Report
April 1, 1964-July 1, 1964
HW-84309, Quarterly Progress Report
July 1, 1964-October 1, 1964

TABLE I
IMPURITY ANALYSIS--TUNGSTEN POWDER
GE Lot # UO.75-4456

<u>Element</u>	<u>ppm</u>	<u>Element</u>	<u>ppm</u>
<u>Spectrographic Analysis</u>			
Al	<6	Ni	30
Ca	11	Cu	<3
Si	<7	Mn	<6
Mo	21	Mg	<3
Fe	5	Sn	<6
Cr	5		
<u>Flame Photometry Analysis</u>			
Na	11		
K	2		
<u>Leco Analysis</u>			
Oxygen	2411		
Nitrogen	106 ± 11		
Carbon	<10		

The hood used for handling the powders and loading and unloading the compacting die is shown in Figure 1. Loose powder was loaded in the mold, plugged at both ends and the mold wrapped with thin plastic and sealed. The material was pressed to 70,000 psi in the container shown in Figure 2. This procedure completely eliminated any contamination outside the hood. Typical as-pressed compacts are illustrated in Figure 3. Total recovery of tungsten plus technetium through the weighing, blending, and compacting was 99.4%.

Arc melting was attempted using as-pressed compacts with a water cooled copper hearth, tungsten electrode, evacuated chamber back filled with argon, and first gettering by melting a zirconium button. The compacts were difficult to strike the arc on, did not conduct well and were gassy in melting. All interior surfaces of the chamber were covered with

a black deposit that made subsequent melting more difficult. It was presumed that oxygen content of the powder, adsorbed gas, and retained gas in the compacts were responsible. The balance of the alloy compacts were loaded in an iron boat in a pyrex tube furnace retort and heated in ultrapurity hydrogen to remove residual moisture and reduce both tungsten and technetium oxides, if present. The temperature was increased slowly over a 4 hr period to 1000 C and held for 1 hr and the material was cooled in hydrogen. Moisture formation in the exit gas was observed and subsequent weighing showed a relatively uniform weight loss of about 0.15 g per 35 g compact. Arc melting was accomplished after the hydrogen sintering without difficulty. Weight losses during melting ranged from 0.25 to 1.60 g.

All interior surfaces of the melt chamber were contaminated to a level of about 50,000 counts/min even though intermediate cleaning of the hearth was done between melt batches. The melted buttons were removed in a nonsmearable condition after only surface wiping. The radioactivity level of the alloy buttons is shown in Figure 4. This results predominantly from the Tc^{99} beta activity and is reduced rapidly with distance or easily shielded with plastic.

The hardness of the alloys was taken on the as-cast buttons and is shown in Figure 5. An initial decrease in hardness is shown with a minimum at 2.5 to 3.5 at.% Tc. Similar results have been observed from rhenium additions in tungsten, molybdenum, and chromium^(1,2) and are attributed primarily to a reduction in interstitial solubility. Further additions of technetium cause an increase in room temperature hardness, presumed to be due to solid solution hardening. In the range of 30 to 40 at.% Tc a change in the hardness curve is noted that probably represents the extent of solid solubility in the nonequilibrium cast structure, with further increases being due to increasing quantities of a second phase in the structure. During load application in the hardness tests with alloys containing 5 at.% Tc or greater audible deformation was noticed, indicating major deformation by twinning. Twinning deformation around a microhardness impression in pure technetium is shown in Figure 8.

The as-cast alloys are shown in Figure 6. A change in surface appearance is noted with even minor technetium additions and this frosty, dull surface is pronounced in alloys of 20 at.% or more. These materials are being prepared for examination of the microstructure, microhardness, X-ray identification of phases present, and fabrication to sheet.

A small quantity of as-hydrogen-reduced technetium powder was mounted in lucite and polished for metallographic examination in attempts to identify any TcO_2 present. No second phase inclusions were observed. The material is a sponge, as shown in Figure 7, not a dense powder. The particle size could no doubt be reduced by grinding.

One of the electron beam melted pure technetium buttons described in the previous report was prepared for metallographic examination. Wide variation in grain size was observed, largely due to differences in solidification rate produced by a small area in contact with the water cooled crucible. The macrostructure and typical microstructures are shown in Figures 8, 9, and 10. This metal was free of the inclusions observed in unalloyed arc melted technetium in the polished condition. The hardness varied from DPH 108 to 134 (120 average) in contrast to 113-189 (140 average) for the arc melted material. Extensive twinning is again evident in the structure, evidently resulting from cooling stresses. The lattice parameters determined for this sample were $a_o = 2.7414 \text{ \AA}$, $c_o = 4.3997 \text{ \AA}$, and the c/a ratio = 1.604. These values compare favorably with those reported by Niemiec;⁽³⁾ $a_o = 2.714 \text{ \AA}$, $c_o = 4.400 \text{ \AA}$, $c/a = 1.605$.

The same electron beam melted button, approximately 3/8 in. in diameter, was vacuum encapsulated in a heavy walled molybdenum container 1 in. in diameter and 0.850 in. high. This assembly was heated to 1540 C and press forged to 0.375 in. height in one pass. The molybdenum was removed chemically using an acid solution containing 1 part H_2O , 1 part HNO_3 , and 1 part H_2SO_4 by volume. Pure technetium was checked in this solution and was only slightly tarnished. The resulting technetium forging, shown in Figure 11, was approximately 0.082 in. thick with an uneven surface apparently related to the cast grain size. Both surfaces

were ground flat to 0.047 in. thickness using metallographic polishing equipment and the microstructure of one surface was examined. Typical structures are shown in Figures 12 and 13. The metal was only partially recrystallized after this working and those areas of recrystallization occurred primarily along the prior cast grain boundaries and occasionally along twin bands. Tensile fractures occurring near the outer diameter of the forging were predominantly along the prior cast boundaries as illustrated in Figure 13. The metal was not reheated after working and the forging was rapid in cold tools. The polished wafer is being used to measure thermal diffusivity of the metal from room temperature to 500 C.

LITERATURE REVIEW

Reference articles concerning the alloying behavior, properties, or fabrication of technetium are listed below and that material of particular interest to the W-Tc study is reviewed.

1. B. C. Allen and R. I. Jaffee. "The Hardness Behavior of Chromium Alloyed with Group IV-A to VIII Transition Metals," Trans. Am. Soc. Metals, vol. 56, pp. 387-401. 1963.
2. R. I. Jaffee and G. T. Hahn. Structural Considerations in Developing Refractory Metal Alloys, DMIC-182. Battelle Memorial Institute Defense Metals Information Center, January 31, 1963.
3. J. Niemiec. "X-Ray Analysis of Technetium Binary Alloys with Tungsten and Rhenium," Bulletin De L'Academie Polonaise Des Sciences, vol. XI, pp. 311-316. 1963.
4. A. L. Giorgi and E. G. Szklarz. Superconductivity Studies of Nb-Tc and Tc-C Systems, CMB-3-1287. 1964.

The superconducting transition temperature was determined for Nb-Tc alloys covering the entire system. X-ray diffraction is being employed to determine phases present. Technetium metal was held liquid in a graphite crucible at 2400 C for 30 min. X-ray pattern of resulting material was completely FCC with $a_0 = 3.985 \text{ \AA}$ indicating that technetium (unlike rhenium) forms a carbide.

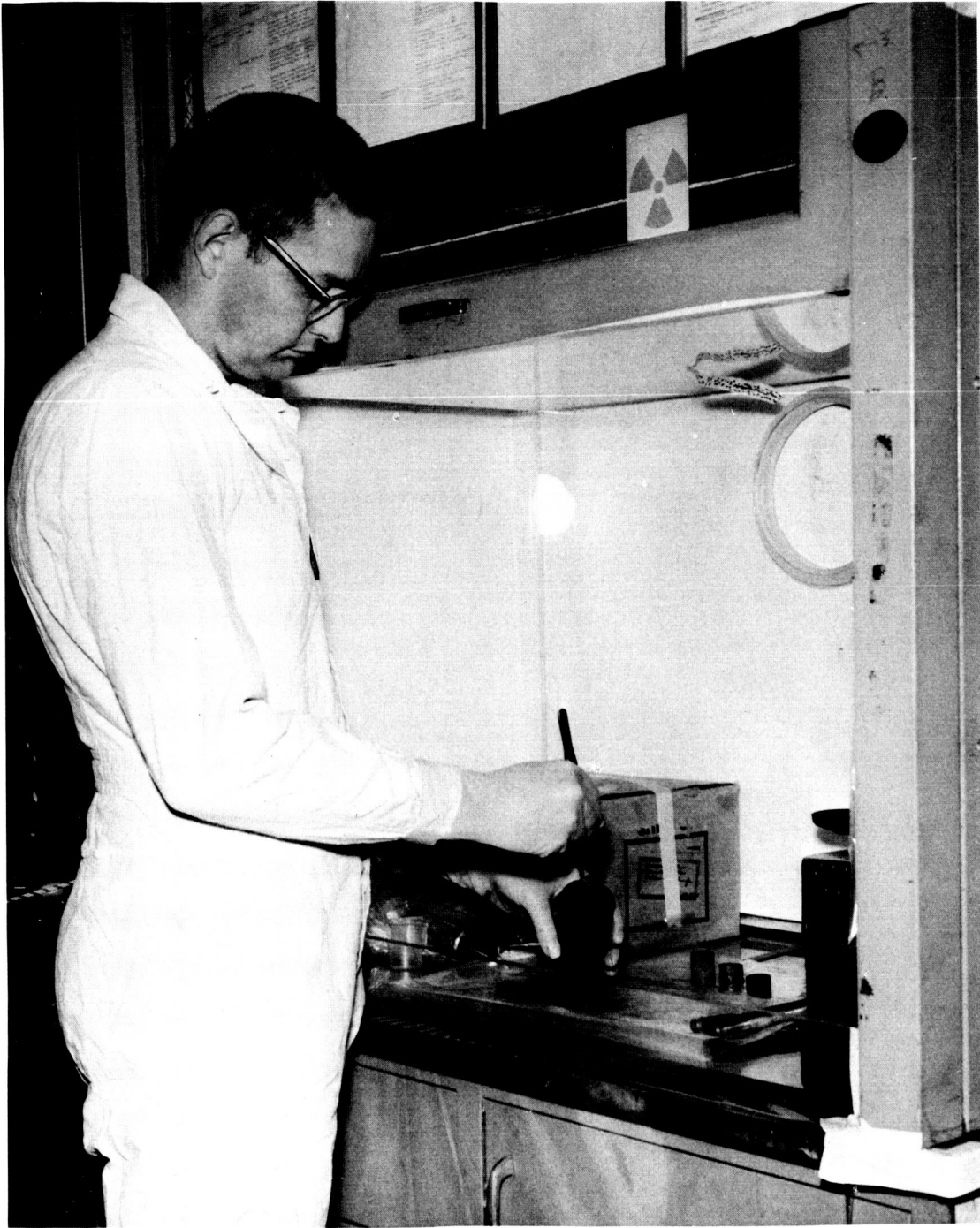


FIGURE 1

Hood Employed for Mixing Tungsten and Technetium Powders, Loading Rubber Compacting Die, and Removing Alloy Compacts



FIGURE 2

750 ton Press Set Up with 2-1/4 in. Container
for Isostatic Pressing W-Tc Powder Compacts

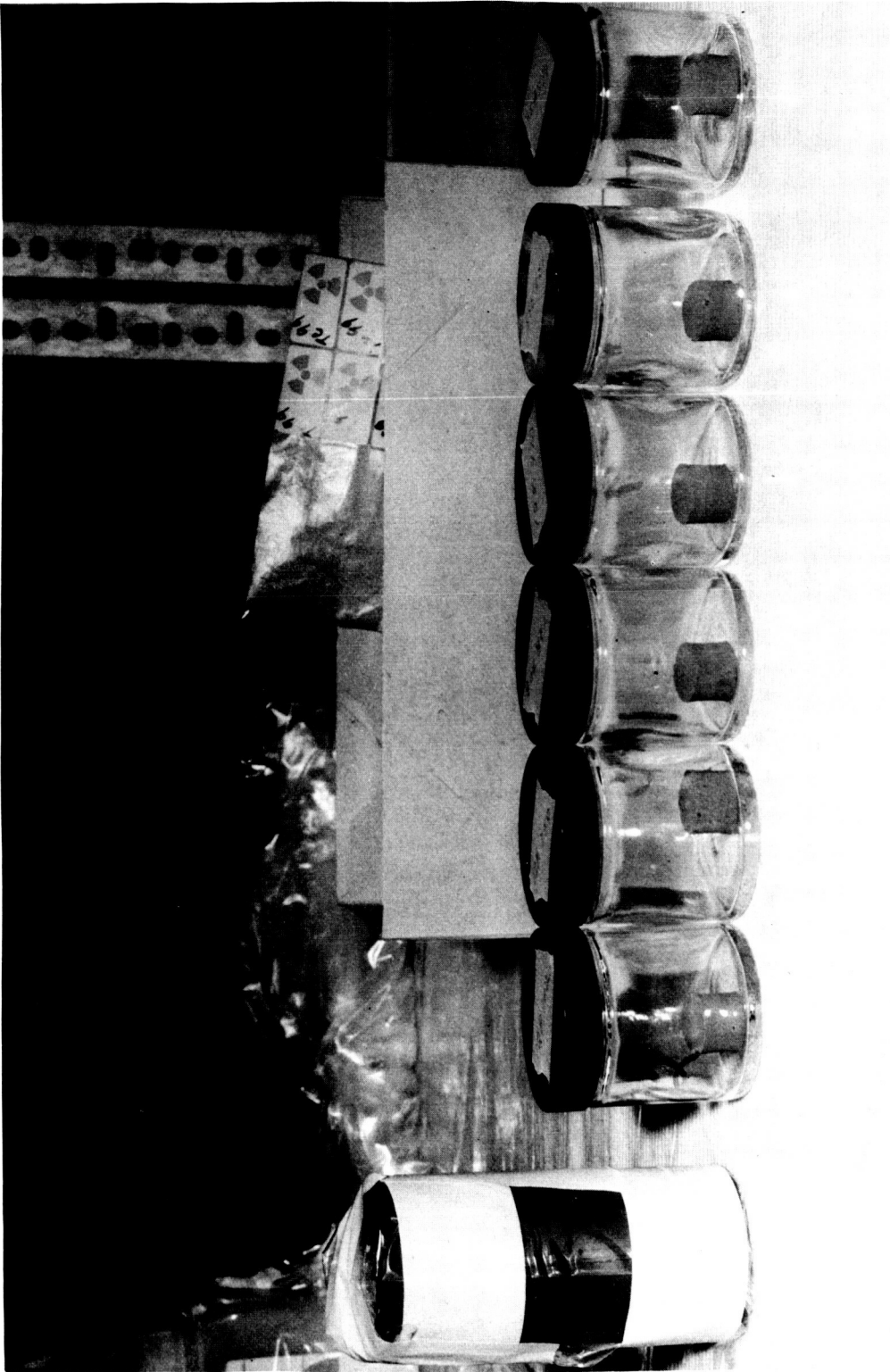


FIGURE 3

W-Tc Powder Compacts
(Note plastic covered compacting die at left.)

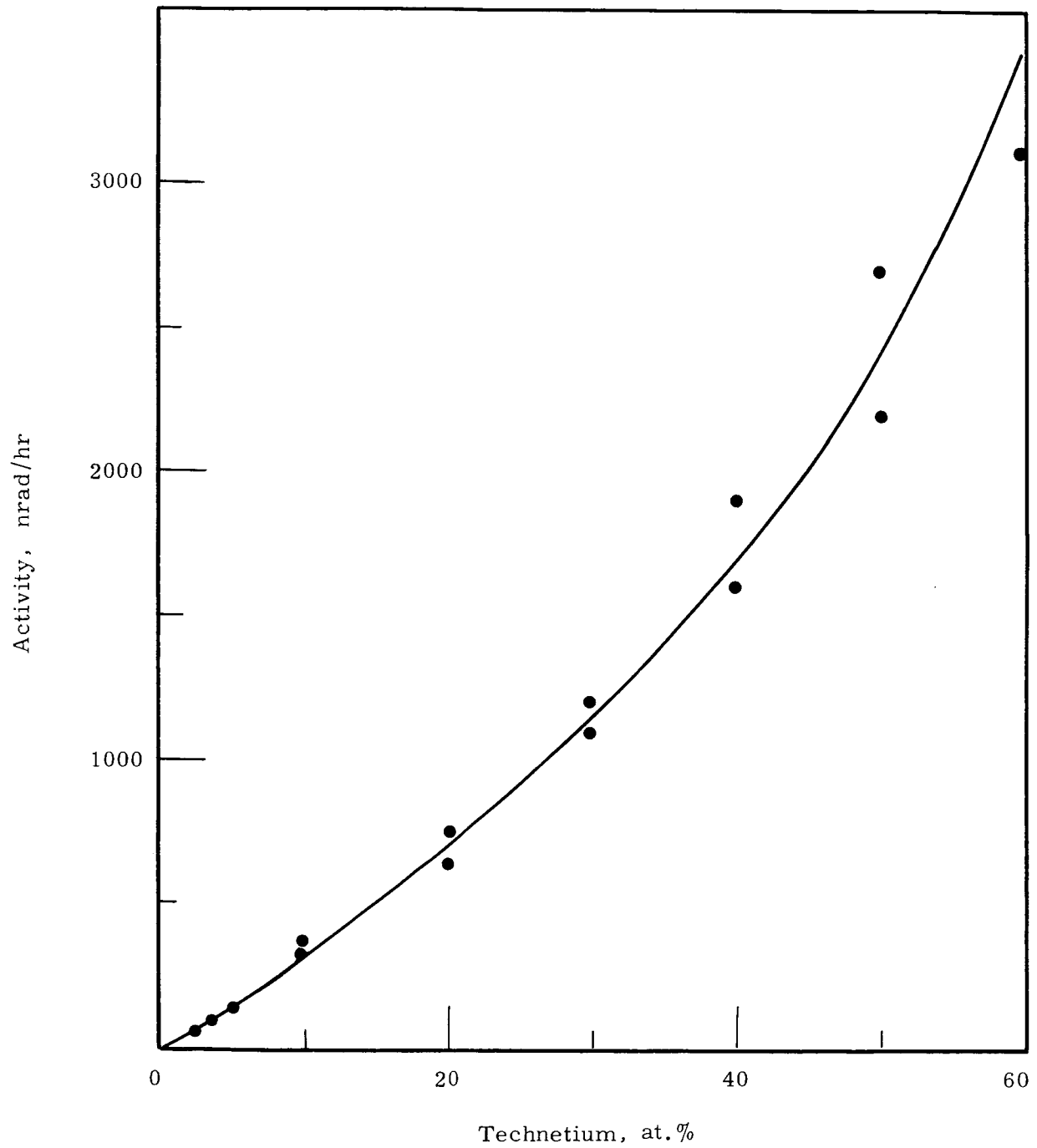


FIGURE 4

Radiation at 2 in. from Surface of 35 g Buttons of W-Tc

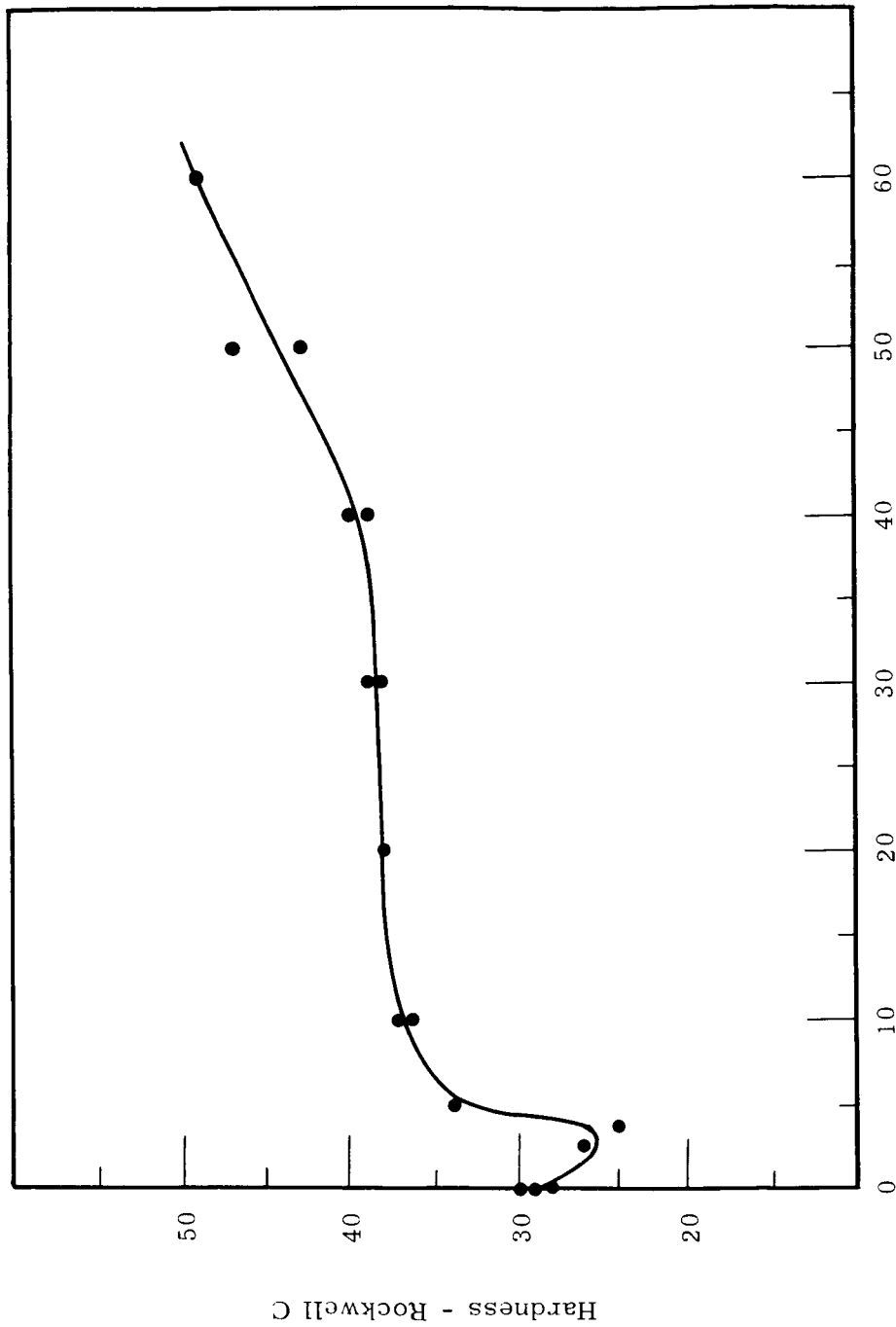
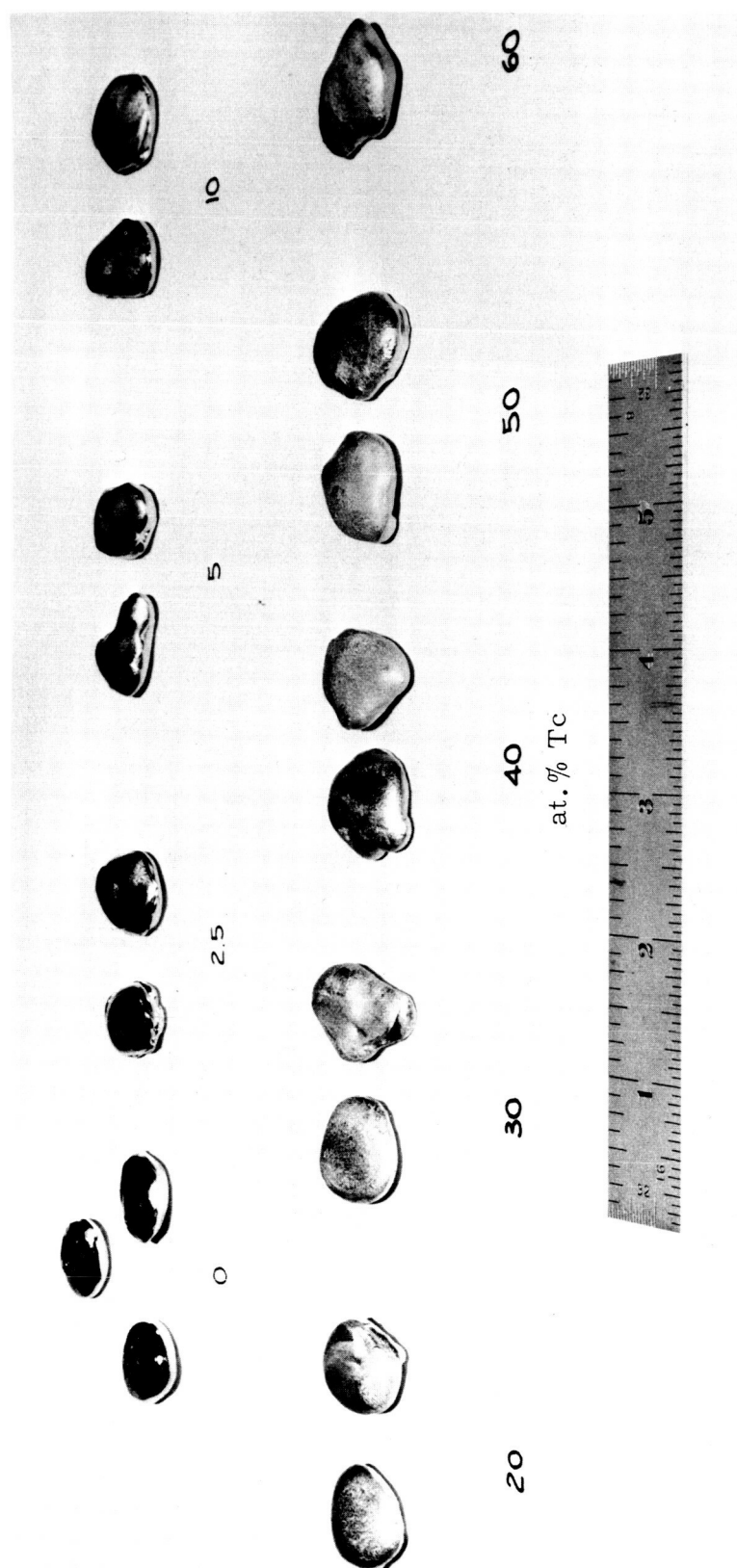
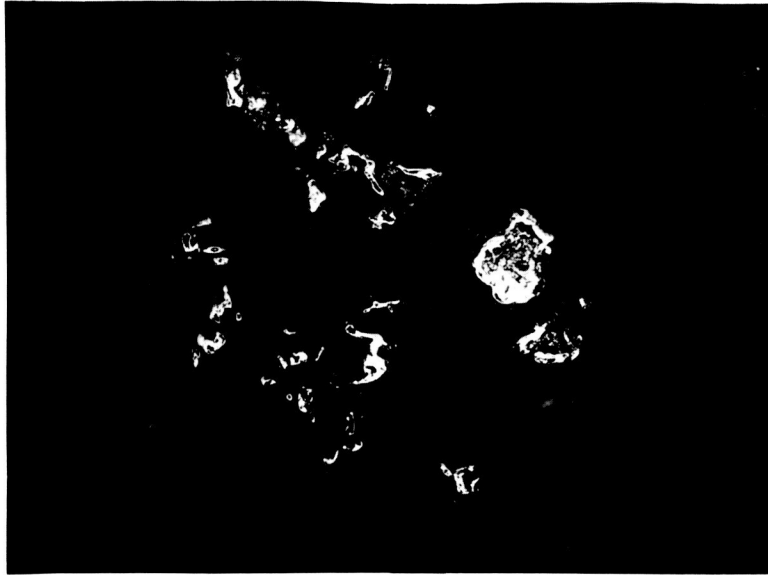


FIGURE 5
Hardness of W-Tc Alloys
(Arc melted buttons)

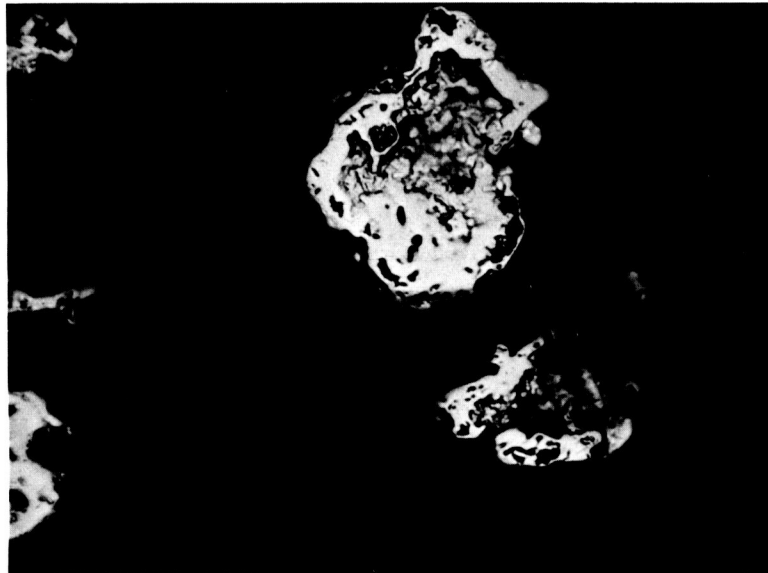


Neg. 0643447

FIGURE 6
Inert Gas Arc Melted W-Tc Alloys



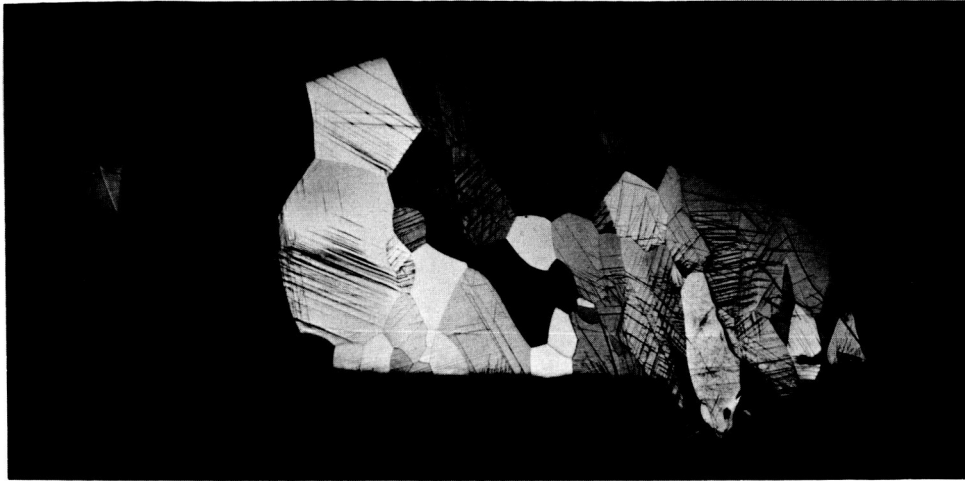
250X



750X

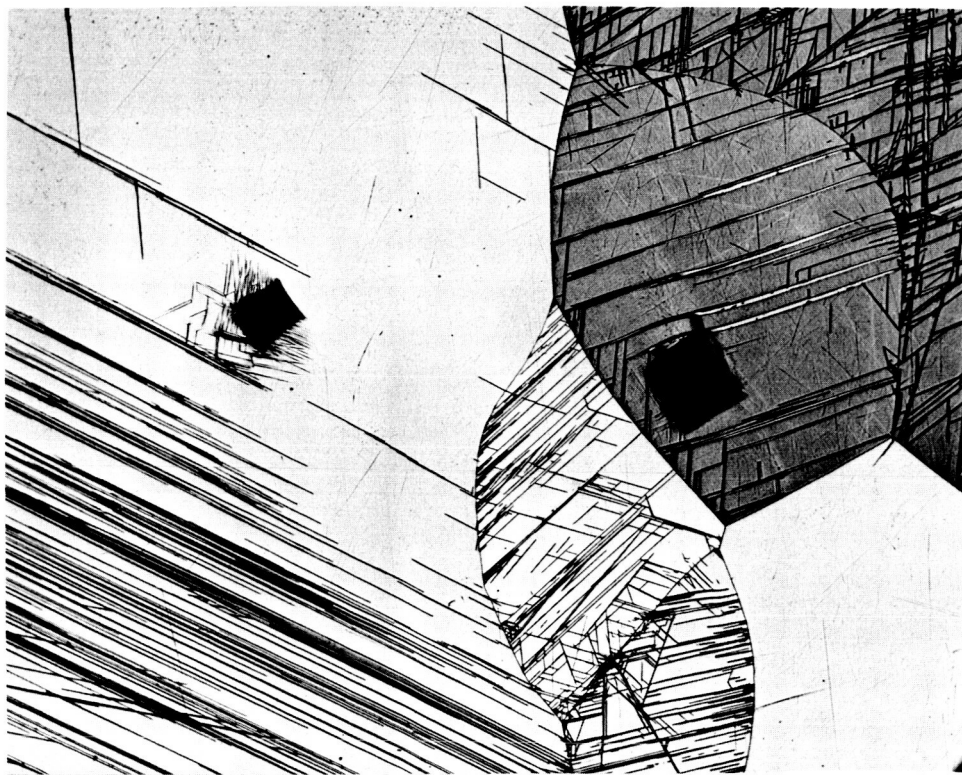
FIGURE 7

As-Hydrogen-Reduced Technetium Powder
Mounted in Lucite and Polished
(Material is a sponge rather than a dense powder.)



Macrostructure

10X



100X

FIGURE 8

Electron Beam Melted Technetium

(Note variation in hardness between grains in lower photograph and the development of twins around hardness impression.)

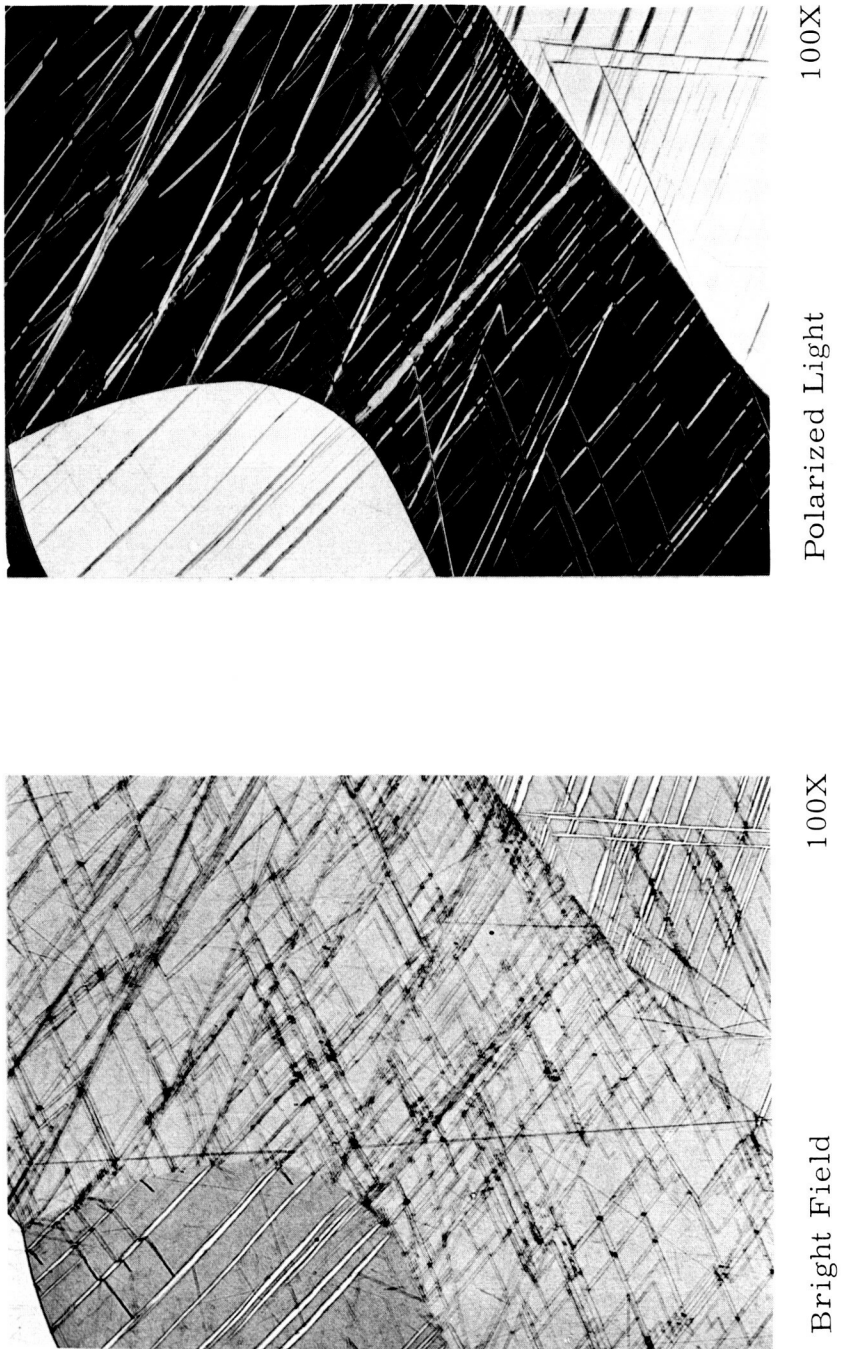


FIGURE 9
Microstructure of Electron Beam Melted Technetium Etched with 10% Oxalic Acid 5 sec at 6 V

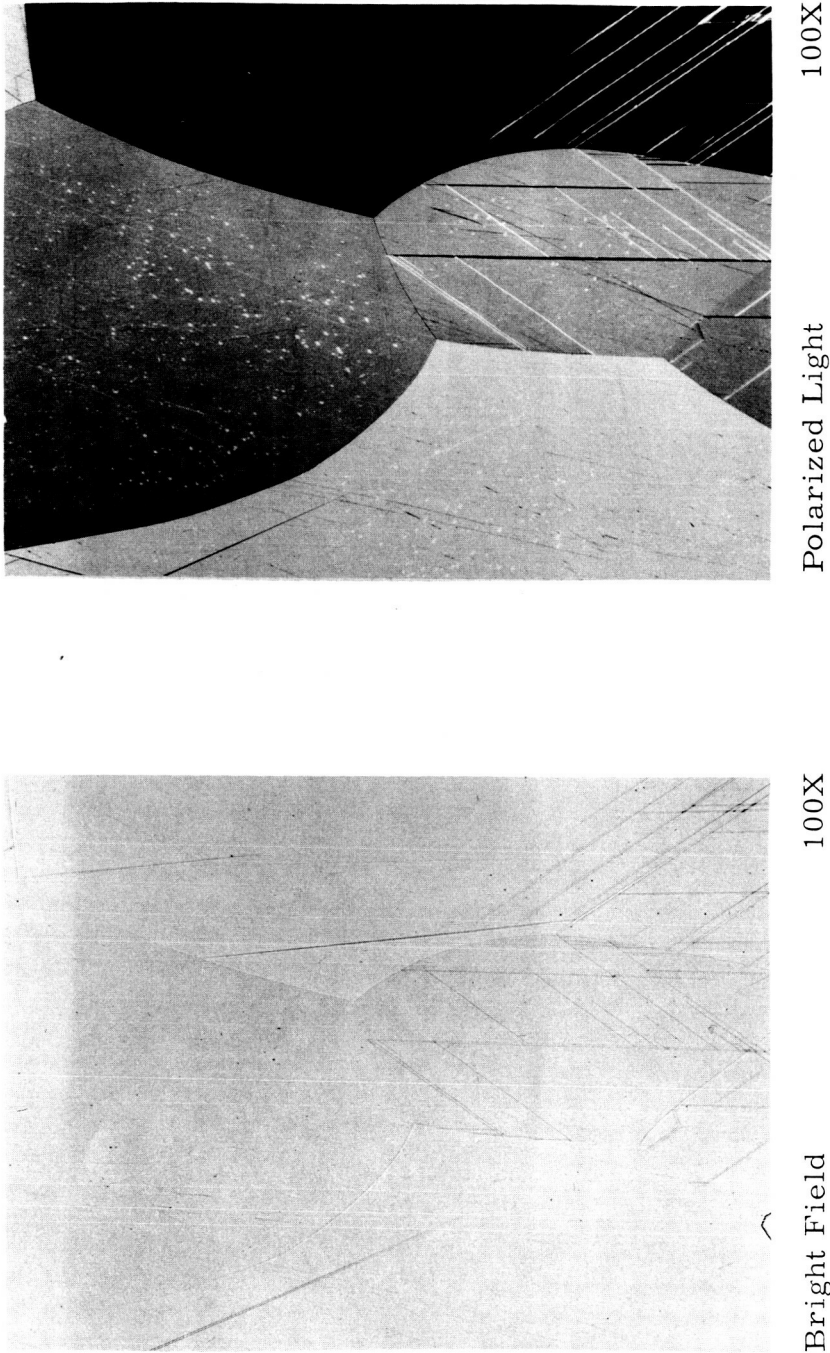
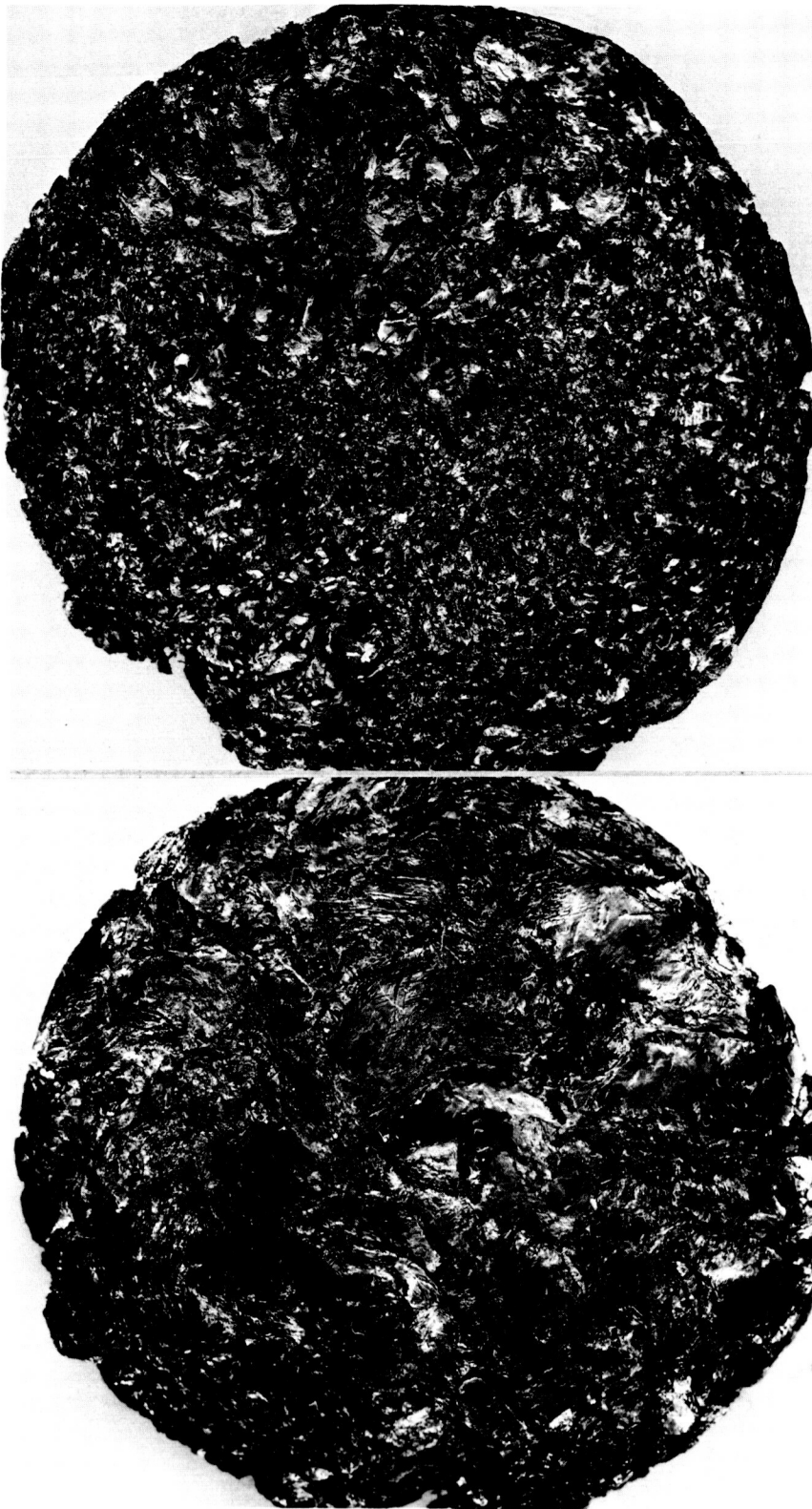


FIGURE 10
 Microstructure of Electron Beam Melted Technetium
 (Phosphoric acid etch* 5 sec at 25 V
 * 8 Parts Ethyl Alcohol
 5 Parts Ortho Phosphoric Acid
 5 Parts Glycerin)

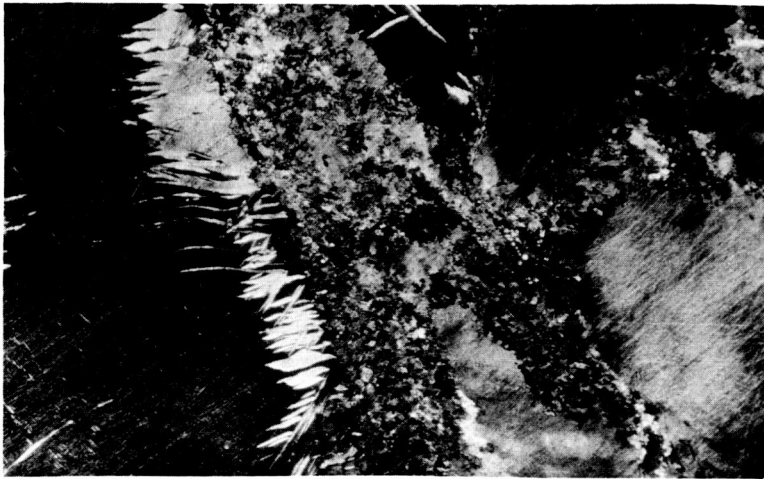


5X

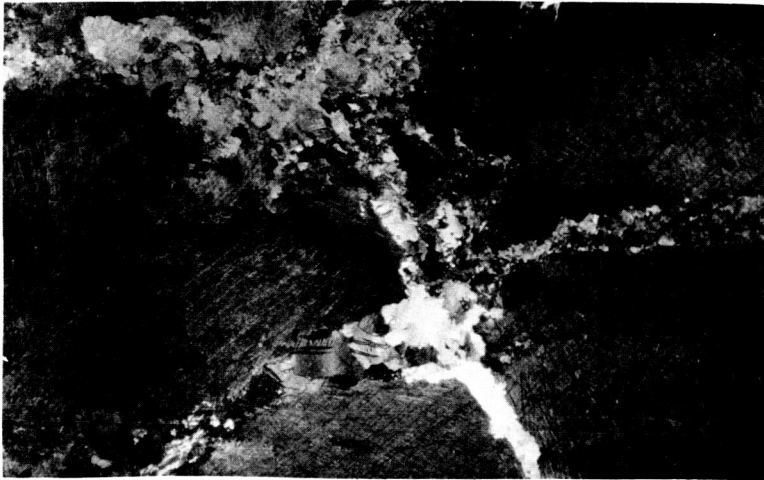
FIGURE 11

Electron Beam Melted Technetium Pellet Approximately 3/8 in. Diameter,
Forged in Molybdenum Capsule to 0.082 in. Thickness at 1540 C

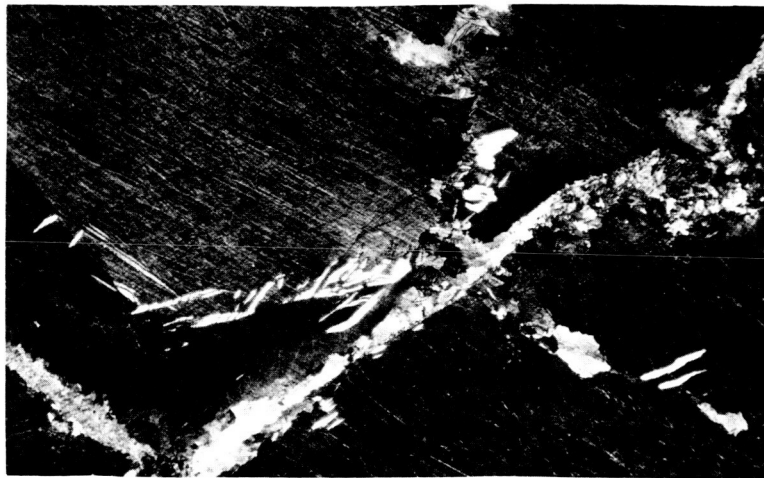
(Left; Top surface of forging, larger grained;
Right; Bottom surface of forging, finer grained in pellet)



100X



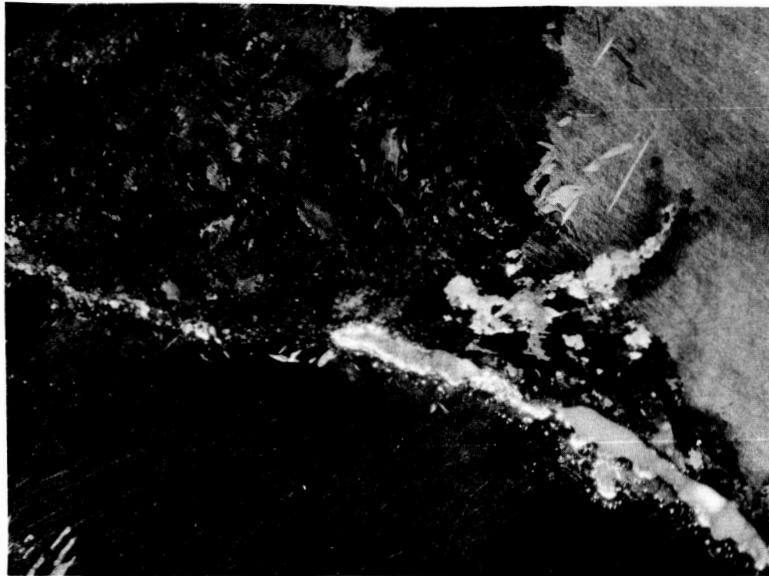
100X



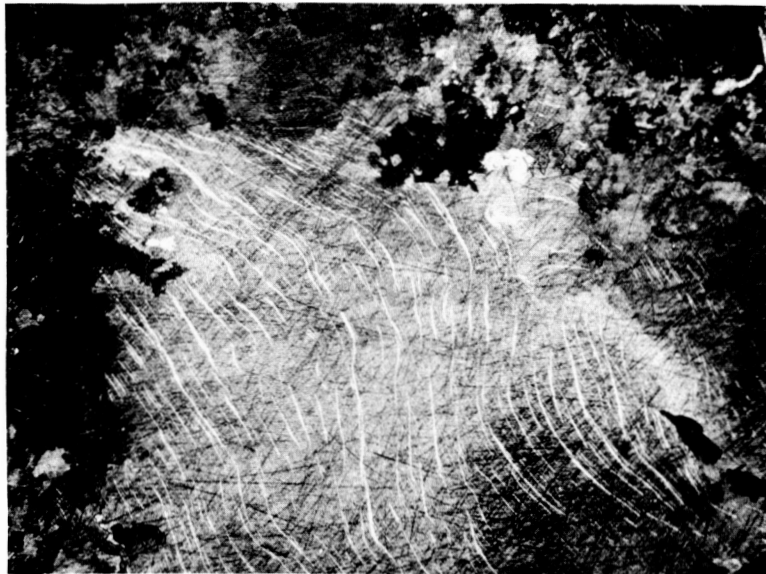
100X

FIGURE 12

Microstructure of Electron Beam Melted Technetium Forged at 1540 C
(Partial recrystallization was observed, occurring predominantly along the cast grain boundaries
and at grain intersections, but occasionally along twin bands as in the left photograph. All
polarized light; etched with 10% oxalic acid.)



100X



100X

FIGURE 13

Microstructure of Electron Beam Melted Technetium
Forged at 1540 C
(Note grain boundary crack in upper photograph
and deformed twins in lower.)

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