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# Oxidation studies of some refractory metals

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IS-854



**IOWA STATE UNIVERSITY**

**OXIDATION STUDIES OF SOME  
REFRACTORY METALS**

by

**James Henry Witte and Harley A. Wilhelm**

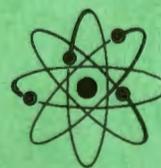
# AMES LABORATORY

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**RESEARCH AND  
DEVELOPMENT  
REPORT**

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IS-854

Metals, Ceramics and Materials (UC-25)  
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Research and Development Report

OXIDATION STUDIES OF SOME  
REFRACTORY METALS

by

James Henry Witte and Harley A. Wilhelm

February, 1964

Ames Laboratory  
at  
Iowa State University of Science and Technology  
F. H. Spedding, Director  
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IS-854

## OXIDATION STUDIES OF SOME REFRACTORY METALS\*

James Henry Witte and Harley A. Wilhelm

## ABSTRACT

Samples of niobium, tantalum, molybdenum and tungsten metals have been given phosphided cases by heating in a phosphorous atmosphere. The samples were subsequently exposed to air at an elevated temperature. In tests at 800°C, the phosphided samples resisted air oxidation markedly compared to the pure untreated samples. The phosphided cases were only a few microns thick yet oxidation resistance of all these samples extended for several hours. Phosphided samples with 90° edges did not resist oxidation at the edges as well as rounded edge samples.

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\*This report is based on an M. S. thesis submitted by James Henry Witte, February, 1964, to Iowa State University, Ames, Iowa.

## I. INTRODUCTION

There is an increasing need for high strength materials that will withstand oxidizing atmospheres at the higher temperatures required for the operation of power generators designed for increased thermal efficiencies desired in atomic, space and conventional engines. A great majority of the refractory metals (those having desirable high-temperature strength) will not withstand an oxidizing atmosphere for any appreciable length of time at temperatures as low as 1000°F. It is known that many alloys are less susceptible to oxidation than their basic components. There is the possibility then of treating a refractory metal to obtain an oxidation resistant composition on its surface. The present investigation is based on a study of the formation of case-phosphided metals and on a study of the oxidation resistance of such treated metals.

Due to the breadth of these areas of study, the present investigation has been limited to the phosphiding of the refractory metals niobium, tantalum, molybdenum and tungsten and to the oxidation behavior of the treated and untreated metals. For the purpose of obtaining an indication of the effectiveness of the phosphiding treatment on these metals oxidation tests were made in a stream of dry air at a temperature of 800°C (1470°F).

## II. HISTORICAL AND LITERATURE SURVEY

In recent years work toward the development of high strength materials that will withstand an oxidizing atmosphere at elevated temperatures has been conducted in many laboratories. The oxidation behavior and other

characteristics of a number of metals have been extensively studied (1, 2, 3). Four refractory metals, niobium, tantalum, molybdenum and tungsten have been most prominent in such studies. However, very little information relative to the preparation and oxidation behavior of phosphided cases on these four metals could be found in the literature.

Phosphide cases have been prepared on a number of metals by the direct reaction of elemental phosphorus vapor on the massive metal. Investigators at the Nuclear Corporation of America (4) have prepared phosphide cases on sheets of four refractory metals, yttrium, zirconium, hafnium and molybdenum by this means at temperatures ranging between 600° and 1000°C. Although the phosphiding treatment was for periods of up to 20 hours, no values of total phosphorus pick up or phosphide case thickness were reported.

Powdered metal phosphides have been prepared by reaction of the powdered metal with phosphine (5). It appears then that phosphide cases could also be prepared by the use of phosphine on massive metal.

The refractory metals with phosphide cases prepared by workers at the Nuclear Corporation of America were tested in an oxidizing atmosphere at 1000°C. It was found that phosphiding decreased the rate of oxidation for short periods of time at this temperature. For molybdenum the period of depressed oxidation was about 3 hours. In the case of yttrium and hafnium the decreased rate lasted about 8 hours and for zirconium about 16 hours (4).

The oxidation behavior of the untreated refractory metals of interest here has been found to follow certain relationships that depend on the

temperature range of oxidation. The rate relationships used to describe most oxidation behaviors are of the general form  $(\Delta m/a)^n = Kt$  (6) where  $\Delta m/a$  is weight gain or loss per unit area, in time  $t$  at temperature, and  $K$  is a constant that depends on the metal and its environment. The value of  $n$  may or may not be a constant for a metal over a range of temperatures.

No such mathematical relationship was proposed in the report of the Nuclear Corporation of America for expressing the oxidation behavior of phosphided metals. The data supplied in the report are inadequate for the period of depressed oxidation to uniquely define the behavior mathematically. It is possible that after the period of depressed oxidation, the behavior resembles that of the untreated metal.

The form of the rate relationship is determined by the numerical value of  $n$ . In the case of a linear rate relationship the value of  $n$  is one, for parabolic and cubic the values of  $n$  are two and three respectively. When  $n$  varies between one and two over a temperature range the behavior is described as a combination of linear and parabolic (6).

The relationship that best represents the oxidation behavior of niobium is parabolic at temperatures not above 300°C. The oxidation behavior transforms to a linear relationship at temperatures of 700°C and greater, a combination of the parabolic and linear applies in the 300° to 700°C (7).

The oxidation behavior of tantalum transforms from parabolic at temperatures below 500°C to linear at temperatures of 700°C and above. Between 500° and 700°C the oxidation is a combination of parabolic and

linear relationships (8).

When molybdenum oxidizes it forms a volatile oxide and loses weight with an increase in time. Thus, the value of  $\Delta m/a$  for molybdenum is negative. However when the oxidation rate relationship is formulated only the absolute value of  $\Delta m/a$  is employed. The oxidation of molybdenum follows a parabolic relationship at temperatures not above 275°C. From 275° to 700° a combination of parabolic and linear relationships is observed and above 700°C the oxidation follows linearity (9).

The oxidation of tungsten is essentially parabolic in nature at temperatures below 500°C. Above 700°C the rate relationship follows a combination of parabolic and linear relationships. Between 500° and 700°C the behavior is not clearly defined (10).

### III. MATERIALS

The elemental materials, niobium, tantalum, molybdenum and tungsten in this investigation were obtained from commercial sources. The metals are all considered as highly refractory. They are all silvery in color and have a common crystal structure, that is, body centered cubic. Some data on these metals are given in Table 1.

Table 1. Some data on refractory metals

Metal	At. no.	At. wt.	Density (g/cm <sup>3</sup> )	a( Å )	m. p. (°C)
Nb	41	92.91	8.55	3.3007	2415
Ta	73	180.95	16.6	3.3026	3097
Mo	42	95.95	10.2	3.1466	2625
W	74	183.86	19.3	3.1648	3370

The niobium metal used in this investigation was a high purity grade (Lot D-3-214) in the form of small beads, obtained from duPont. The analytical data supplied by duPont for this lot of niobium are shown in Table 2.

Table 2. Impurities in duPont niobium

Impurity	Impurity concentration
Ta, Fe, Cr, Ni, Ti	200 PPM total
O	200 PPM
N	30 PPM
C	30 PPM
W	200 PPM

The tantalum used in this investigation was obtained from the Fansteel Metallurgical Corporation in the form of one-fourth inch diameter rod. No analysis was obtained with the shipment; however an analysis was performed by spectrographic means at Ames Laboratory and the results are shown in Table 3.

Table 3. Impurities in the Fansteel tantalum

Impurity	Impurity concentration	Impurity	Impurity concentration
Fe	< 50	Ti	< 50
Mo	<1000	W	<500
Nb	< 30	Zr	400
Ni	< 50	Cr	< 20

The molybdenum used was also obtained from the Fansteel Metallurgical Corporation and was in the form of five-eighths inch diameter rod. The results of a spectrographic analysis made at the

Ames Laboratory of the metal are presented in Table 4.

Table 4. Impurities in the Fansteel molybdenum

Impurity	Impurity concentration	Impurity	Impurity concentration
Fe	<200	Ta	<400
Cr	< 50	Ti	< 50
Nb	< 100	W	<500
Ni	< 50	Zr	<100

The Cleveland Tungsten Corporation was the source of the tungsten used in this study. The tungsten was obtained in the form of one-half inch diameter rod. The results of a spectrographic analysis performed at the Ames Laboratory are shown in Table 5.

Table 5. Impurities in Cleveland Tungsten Corporation tungsten

Impurity	Impurity concentration	Impurity	Impurity concentration
Fe	< 20	Ta	<400
Mo	<300	Ti	< 50
Nb	<100	Zr	<200
Ni	< 50	Cr	< 20

Phosphorus can be obtained in a number of allotropic forms. The red allotrope was used as the means for supplying the reactant to form phosphide cases on the refractory metals. This particular form of phosphorus is readily available as an amorphous powder. It is easily handled in air with only minor precautions. Phosphorus has an atomic number of 15 and an atomic weight of 30.98. The phosphorus used was of the reagent grade and was obtained from Fisher Scientific Company.

#### IV. SPECIMEN PREPARATION

##### A. Fabrication of the Refractory Metal

Several test samples of each refractory metal were fabricated so that the effect of the phosphide cased metal could be compared with the untreated metal. The series of tests on each metal included phosphided samples having somewhat rounded corners and samples having roughly 90° corners. The test samples of the metals were fabricated from the stock described in the section on materials, and were made in such dimensions that they could be introduced into the phosphiding chamber which was a 13 mm I. D. vycor tube. All samples were ground, after shaping, to a 600 grit finish by using a series of silicon carbide papers from 240 to 600 grit. Holes were drilled, in the shaped and ground specimens, near one edge of each piece to accept the support wire.

The niobium in bead form was consolidated by nonconsumable arc melting with a tungsten electrode, on a water cooled copper hearth, under one atmosphere of argon. The arc-melted button was then cold rolled to a final thickness of about one-eighth of an inch. Rectangular pieces of approximately three-eighths of an inch by three-fourths of an inch were cut by the use of a silicon carbide abrasion saw. The rough cut pieces were then milled to approach uniformity. The square edged corners on two of the samples were rounded by means of silicon carbide paper.

The tantalum was consolidated and fabricated in the same manner as the niobium; the only difference was the material, which was one-

fourth inch diameter rod.

The five-eighths inch diameter molybdenum rod was sliced into one-eighth inch thick discs. Two edges were then milled on the discs to permit the specimens to enter the phosphiding tube. Silicon carbide paper was used to radius the corners of two specimens.

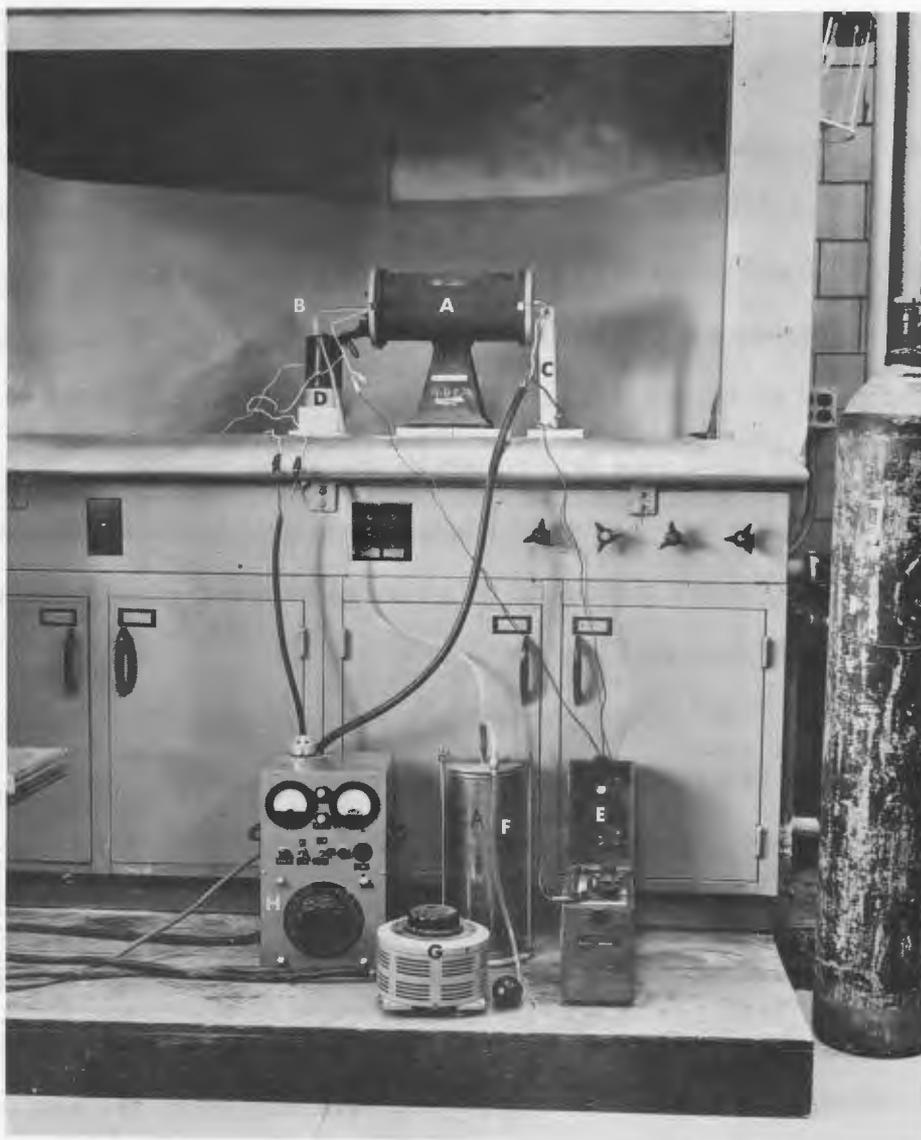
The tungsten used was fabricated in the same manner as the molybdenum but the two flattened edges, required for acceptance into the reaction tube, were produced by grinding instead of milling because of the hardness of tungsten.

#### B. Phosphide Case Preparation

All samples to be phosphided for each metal were treated simultaneously in closed systems consisting essentially of 13 mm I. D. tubes such as that shown in Figure 1.

The reaction tubes, fabricated from vycor tubing, were first sealed on one end and then bent as shown in the figure. About seven grams of the red phosphorus was introduced and then moved to the sealed end of each tube. The metal samples to be phosphided in each reaction tube were then introduced and positioned near the center of the tube. The tube was then evacuated, sealed and placed in the resistance furnace as shown in the figure. This furnace was a wire wound split type (Hevi Duty Electric Company, Type 70) unit having a heating chamber one inch in diameter by 16 inches in length.

A wire wound heater was then placed on the tube at the end containing the phosphorus. The end of the tube emerging from the other end of the furnace was immersed in liquid nitrogen. The center of the reaction



**Figure 1.** Phosphiding apparatus: A. Furnace to heat samples; B. Reaction tube; C. Phosphorus heater; D. Liquid nitrogen container; E. Potentiometer with DPDT switch to measure temperature of furnace and heater; F. Liquid nitrogen storage container; G. Power control for heater; H. Power control for furnace.

vessel containing the metal samples was maintained at  $900^{\circ}\pm 30^{\circ}\text{C}$ , while the end containing the phosphorus was maintained at  $350^{\circ}\pm 10^{\circ}\text{C}$ . These conditions were maintained on the system until all of the phosphorus had moved from its original location. The phosphorus had then moved to the hot zone of the furnace and had either reacted with the metal specimens there or had passed on and condensed at the cold end of the tube. The time usually allowed for the transfer of the phosphorus under these conditions was about seventy-two hours. After this phosphiding treatment the power to the furnace and heater was turned off. After the system had been allowed to come to ambient temperature, the Vycor tube was removed. It was found that a large fraction of the untreated phosphorus in the tube converts during the process to the yellow allotropic form which is quite pyrophoric. The Vycor tube was broken open under water to recover the treated samples. The phosphided samples were then dried with methyl alcohol.

Typical phosphide coated specimens were selected for microscopic examination. The specimens were cut longitudinally and then mounted between two steel plates in order to prevent rounding or flaking at the case during the polishing procedure. The surface to be polished was first ground on 240, 320, 400 and then 600 grit silicon carbide paper. These prepared surfaces were then polished with Line "A" followed by Linde "B" to give a final finish. The polished surfaces were not etched. Photomicrographs were taken of the sections at 500X magnification. The photomicrographs obtained from these sections are shown

in Figures 2-5 and some of the changes in the metal samples due to the phosphiding treatment are shown in Table 6.

Table 6. Some changes in metal samples due to phosphiding treatment.

1. Phosphided metal	Nb	Ta	Mo	W
2. Area of samples (cm <sup>2</sup> )	3.94	4.12	3.93	2.82
3. Phosphorus pick up (gms)	0.0151	0.0070	0.0048	0.0020
4. Measured average depth of case	12 $\mu$	4.0 $\mu$	5.0 $\mu$	4.0 $\mu$
5. Calculated grams P/cm <sup>3</sup> in case (using experimental data)	3.19	4.25	2.44	1.77
6. Assumed case species	NbP	TaP	MoP	WP
7. Density of assumed species (g/cm <sup>3</sup> )	6.52	11.16	7.25	12.33
8. Calculated grams P/cm <sup>3</sup> in case (using assumed species)	1.63	1.63	1.77	1.78
9. Calculated depth of case (using assumed species)	23.5 $\mu$	10.41 $\mu$	6.9 $\mu$	4.0 $\mu$

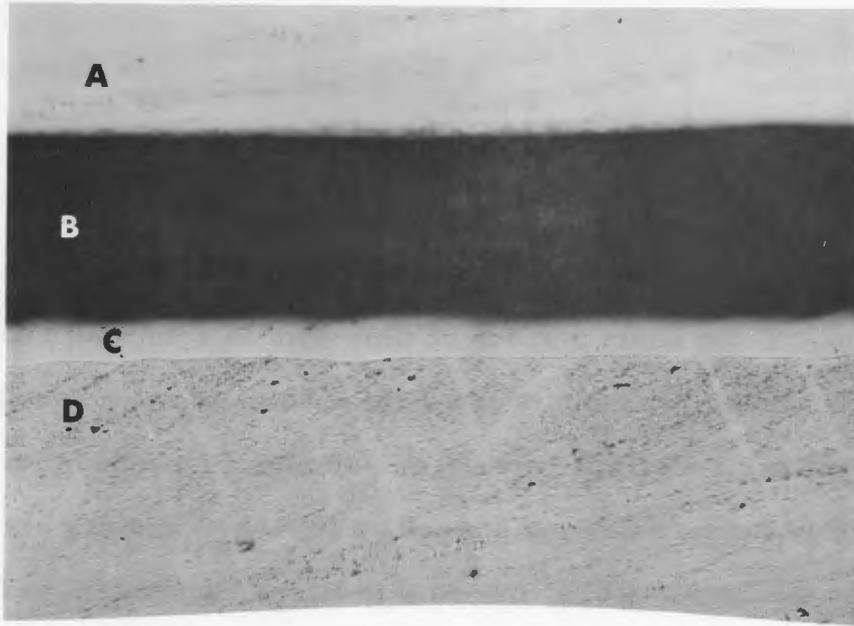
Comparisons of the values in lines five and eight show that the observed weights of phosphorous per unit volume check fairly well with the calculated values based on crystal data only for the monophosphides of tungsten and molybdenum. In the cases of niobium and tantalum the experimental phosphorous contents per unit volume appear to be roughly double those calculated for their monophosphides. Comparisons of the values in lines four and nine give another means of interpreting the data on phosphiding these metals. It appears then that the metal-phosphorous atom ratios in the phosphided cases correspond roughly to NbP<sub>2</sub>, TaP<sub>2</sub>, MoP and WP.

## V. OXIDATION TESTS

Some of the molybdenum samples were exposed to air in a muffle furnace at 800°C for short periods of time with intermittent cooling for weighing. However most of the data on oxidation were obtained with an automatic recording balance on samples suspended in a furnace. This furnace was maintained at  $800^{\circ} \pm 5^{\circ}\text{C}$  and dry air was passed over the samples at a flow rate in liters, equivalent to 0.45 liters at standard temperature and pressure, per minute. The furnace temperature was controlled by a Leeds and Northrup series 60 control unit and was recorded on a Speedomax H. The air supply was regulated by a needle valve and measured by a Matheson rotameter. The air was dried by a series of two sulfuric acid bubblers and two drying columns containing indicating Dryrite.

The changes in weights of the samples during these air oxidation tests were recorded continuously on the Ainsworth recording macro-balance type AV-AU-1 shown in Figure 6.

A Vycor tube, 47 mm I. D. by 36 inches in length, sealed at one end and fitted with a Cenco screw-on connector at the other end, served as the oxidation test chamber. This tube was connected to the balance chamber through a copper tube adapter approximately two inches I. D. by 22 inches in length. This adapter was designed to permit evacuation of the system or the introduction of gas (in this case air) to the bottom of the test chamber and also accommodate lead wires from the



**Figure 2.** Photomicrograph of a niobium phosphide case taken at 500X magnification: A. Steel plate; B. Gap; C. Niobium phosphide case; D. Niobium base metal.



**Figure 3.** Photomicrograph of a tantalum phosphide case taken at 500X magnification: A. Steel plate; B. Gap; C. Tantalum phosphide case; D. Tantalum base metal.

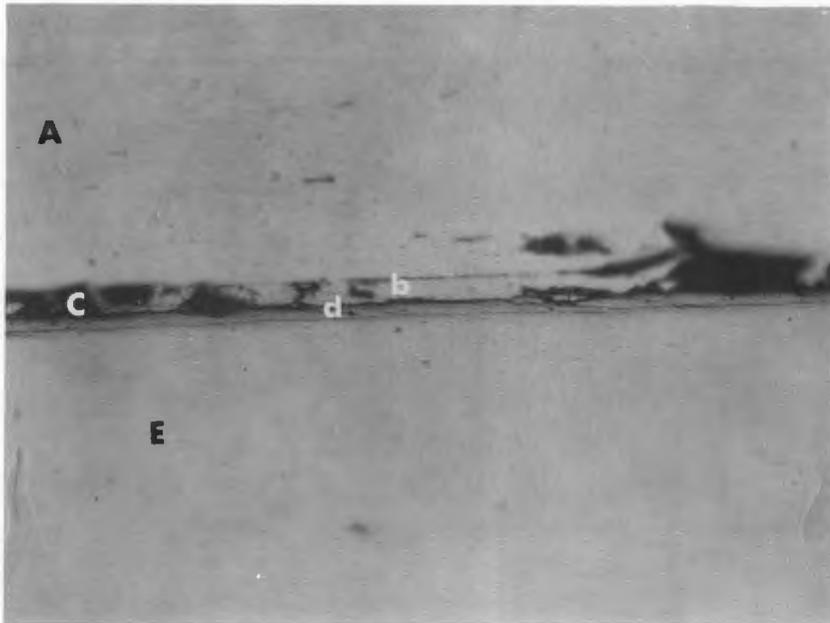


Figure 4. Photomicrograph of a molybdenum phosphide case taken at 500X magnification. A. Steel plate; B. Polishing compound; C. Gap; D. Molybdenum phosphide case; E. Molybdenum base metal.



Figure 5. Photomicrograph of a tungsten phosphide case taken at 500X magnification. A. Steel plate; B. Polishing compound; C. Gap; D. Tungsten phosphide case; E. Tungsten base metal.



Figure 6. Oxidation test apparatus: A. Balance; B. Adapter (detailed in Figure 7); C. Oxidation test chamber; D. Furnace; E. Weight change recorder; F. Furnace temperature controller and recorder.

thermocouple, located near the test sample, to the temperature controller and recorder. Figure 7 shows in some detail the design of this adapter.

The samples were suspended in the furnace tube by means of a platinum chain attached to a saddle at one end of the beam of the recording balance.

The recording device for the balance indicated weight change horizontally as the chart paper was driven vertically at a fixed rate of 1.5, 6 or 12 inches per hour depending on the test being made.

## VI. RESULTS

The data obtained from the recorder were replotted as the weight gain per unit area against time at temperature as shown in Figures 8-11. The data were again plotted as the log of time against the log of weight gain per unit area to determine whether changes in slope (Figures 8-11) were linear functions. The log of time against log of weight gain are straight lines the equation  $(m/a)^n = Kt$  may be employed to represent oxidation behavior.

In order to apply this equation for a sample the values of  $n$  and  $K$  must be determined. The value of  $n$  may be determined mathematically from the original expression. For two relevant points

$$(\Delta m_1/a)^n = Kt_1 \text{ and } (\Delta m_2/a)^n = Kt_2.$$

The above expression rewritten in log form,  $n \log (\Delta m_1/a) + \log t_2 = n \log (\Delta m_2/a) + \log t_1$ , then solved for  $n$  yields  $n = \frac{\log (t_1/t_2)}{\log \frac{\Delta m_1}{a} - \log \frac{\Delta m_2}{a}}$ .

Values of  $\Delta m_1/a$  and  $\Delta m_2/a$  and their corresponding values of  $t_1$  and  $t_2$  were taken at the limits of the straight line portion of a plot. These

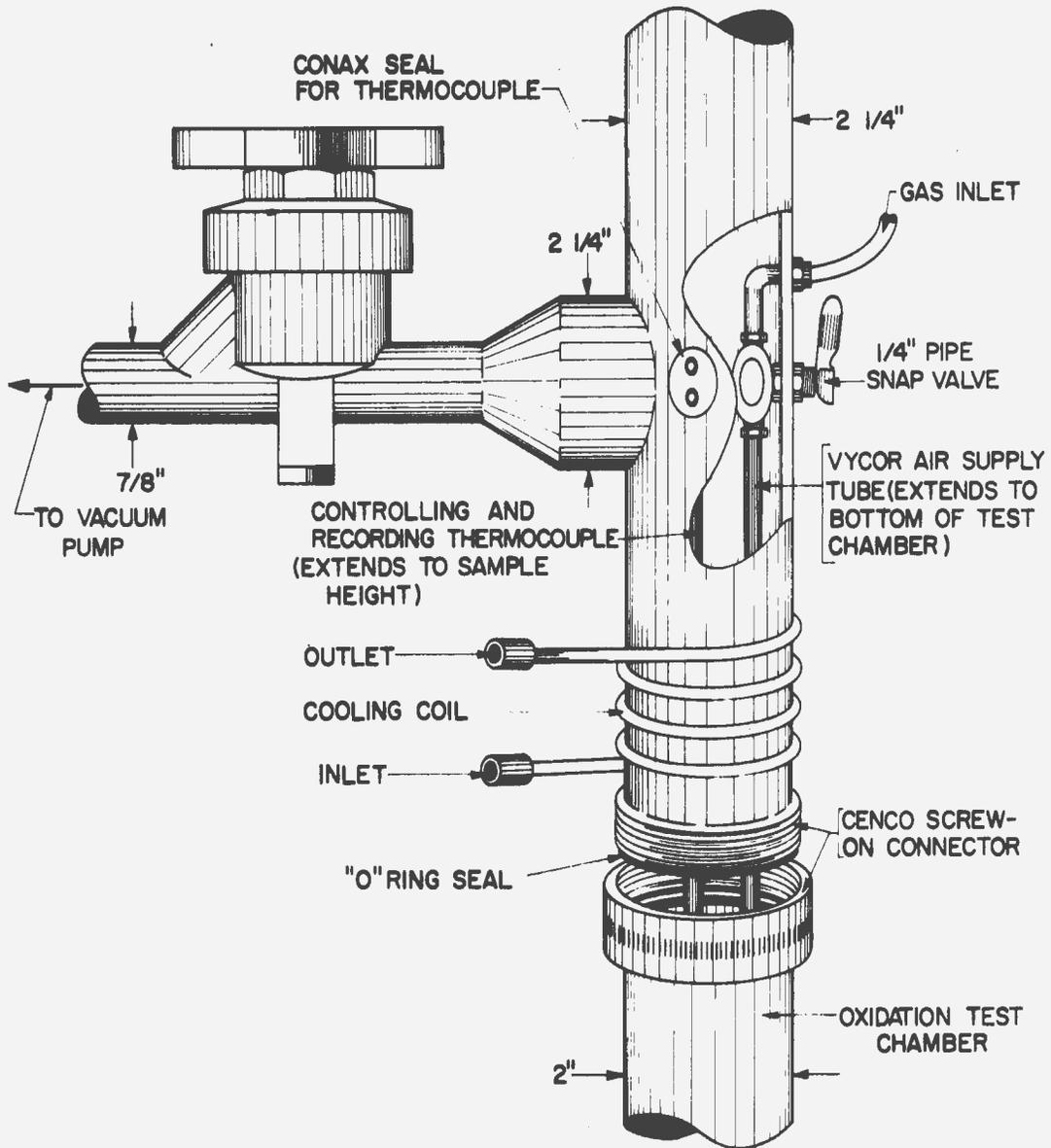


Figure 7. Adapter

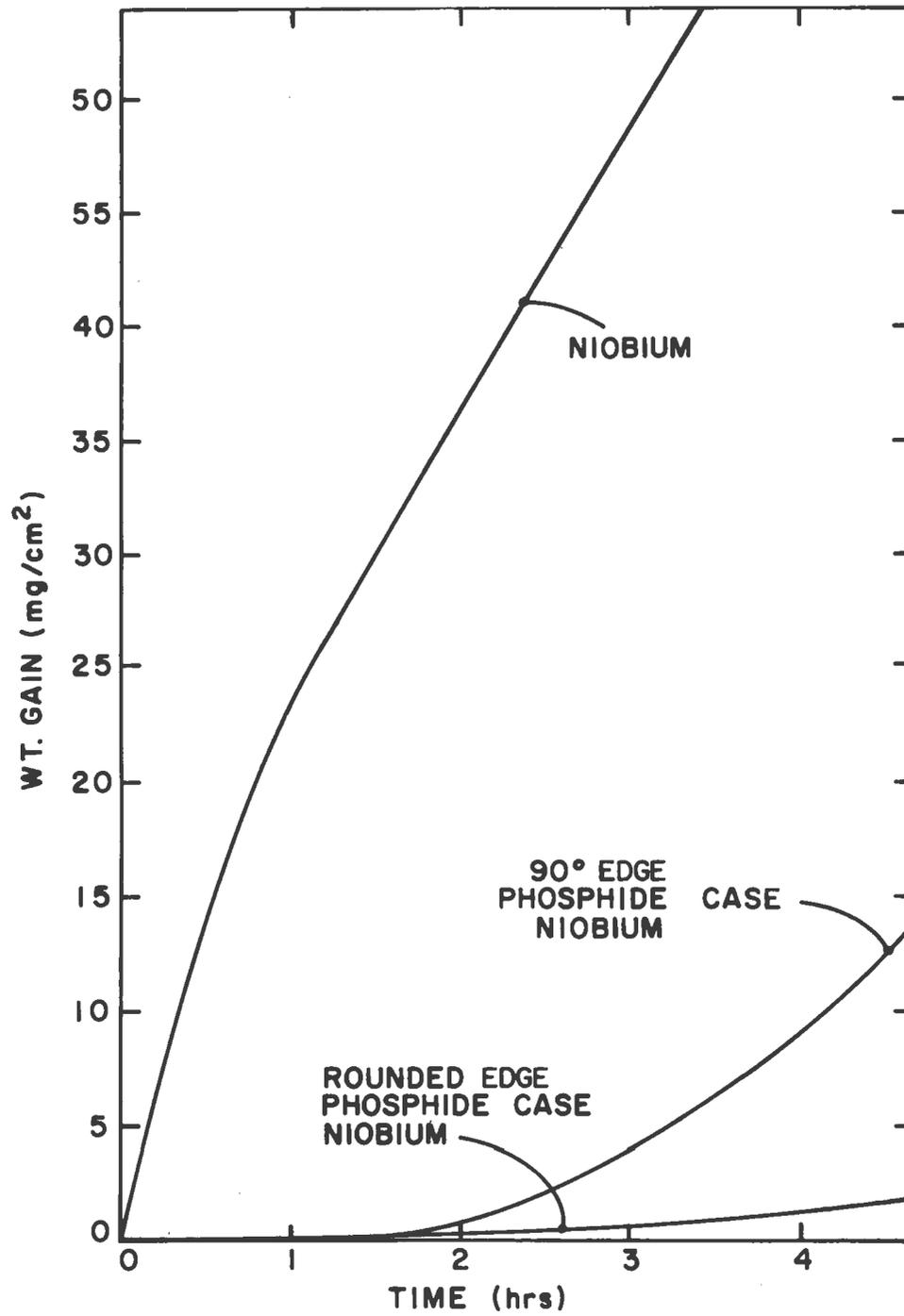


Figure 8. Plots of weight gain per unit area against time for niobium and average values for niobium phosphide cased samples

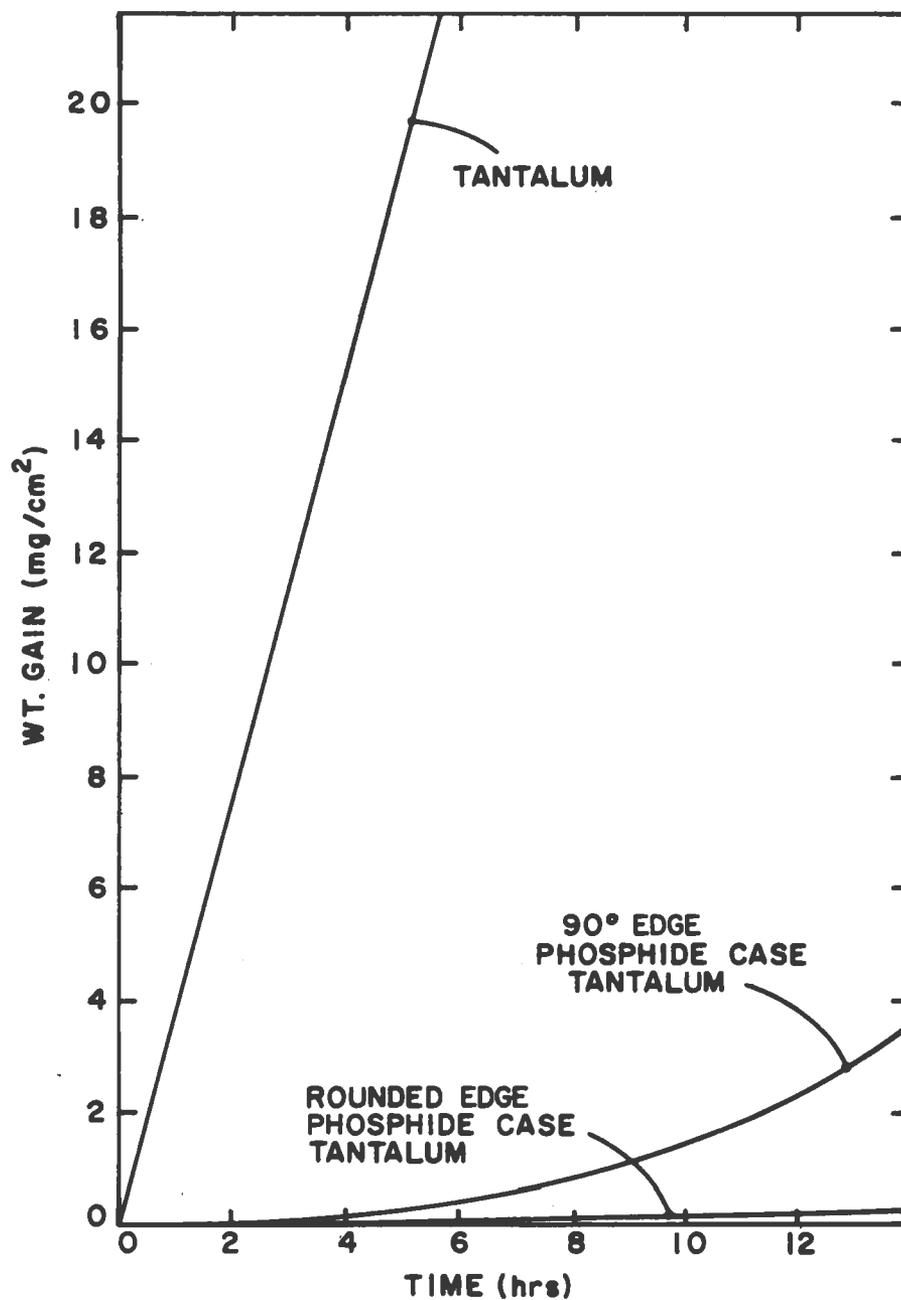


Figure 9. Plots of weight gain per unit area against time for tantalum and average values for tantalum phosphide cased samples

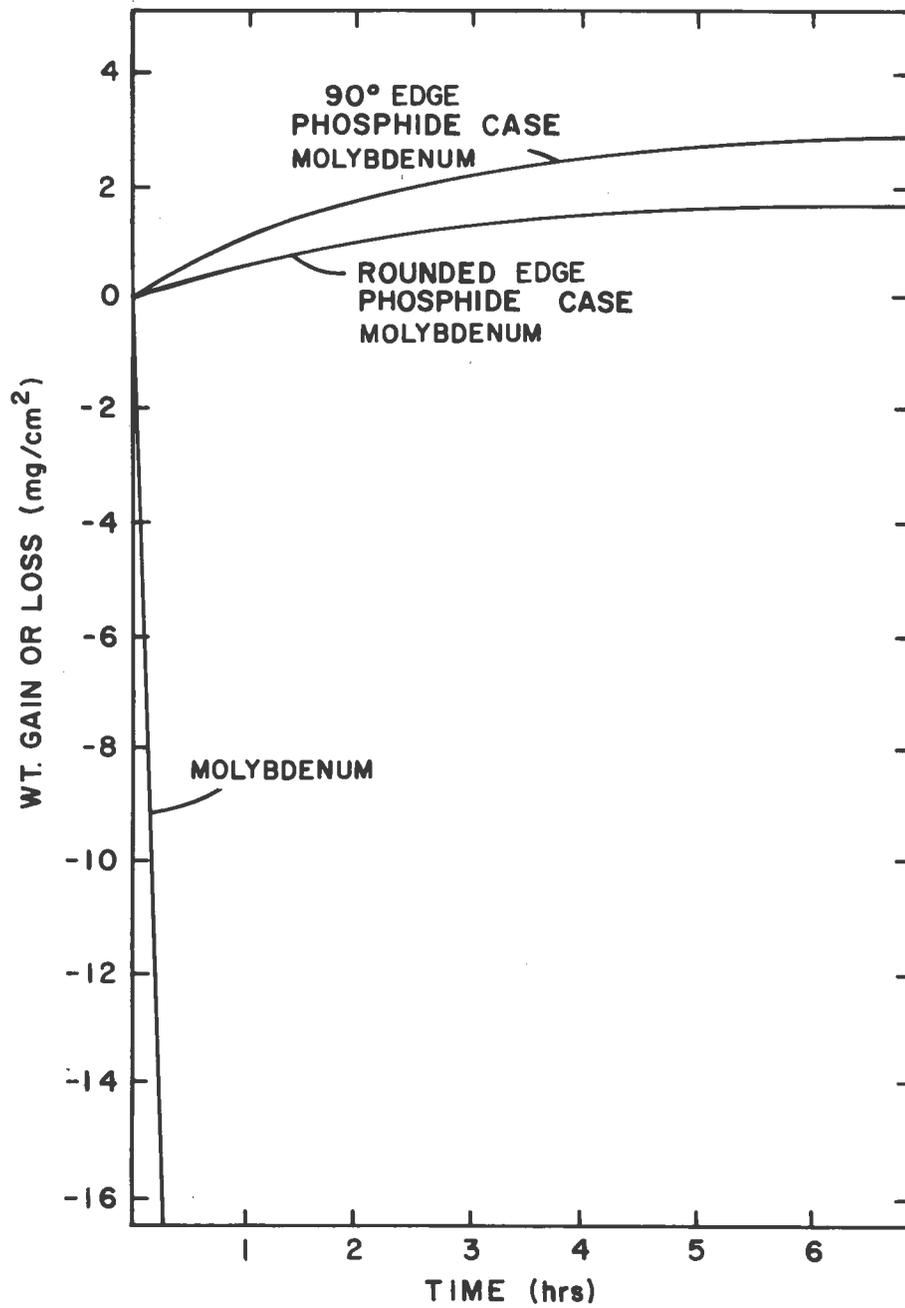


Figure 10. Plots of weight gain per unit area against time for molybdenum and average values for molybdenum phosphide cased samples.

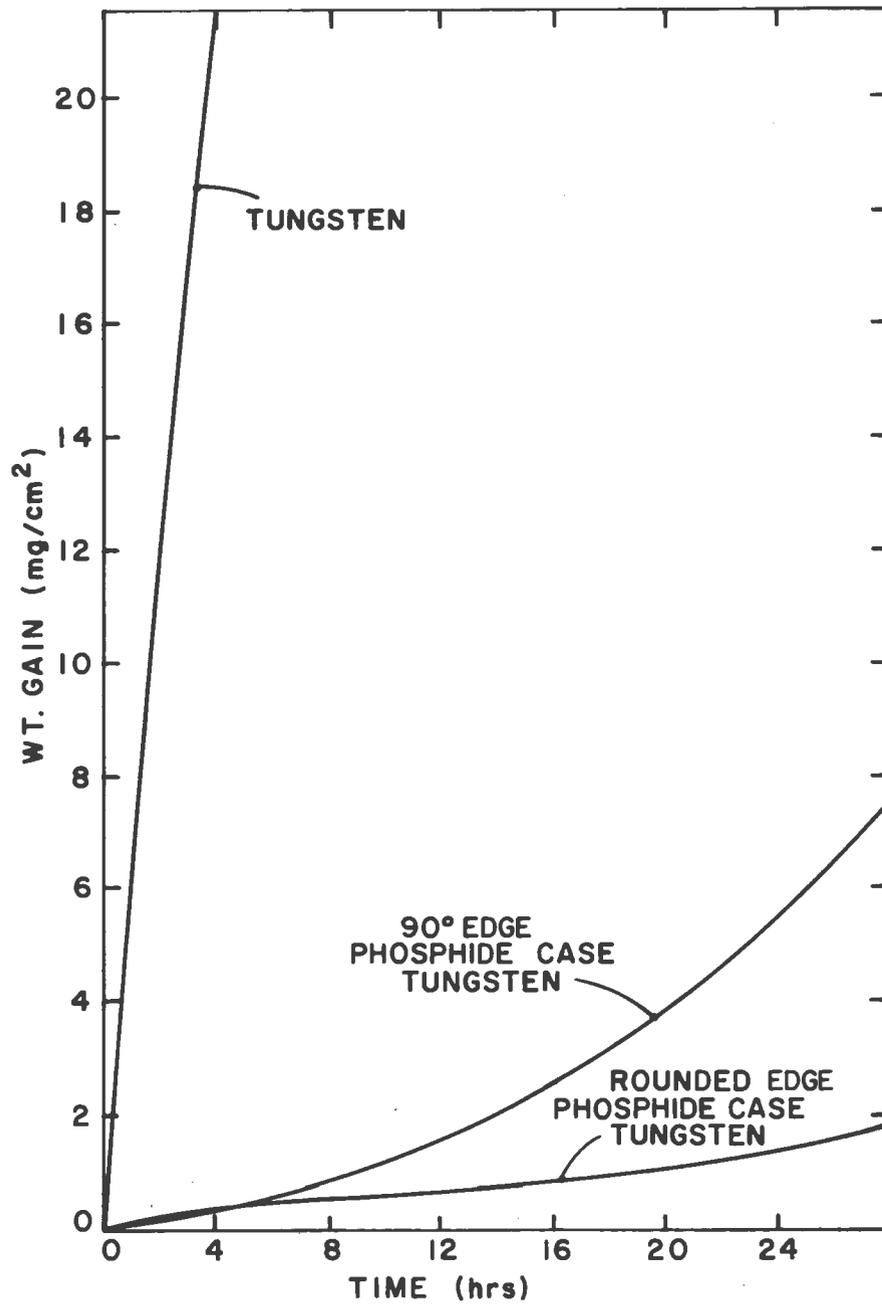


Figure 11. Plots of weight gain per unit area against time for tungsten and average values for tungsten phosphide cased samples

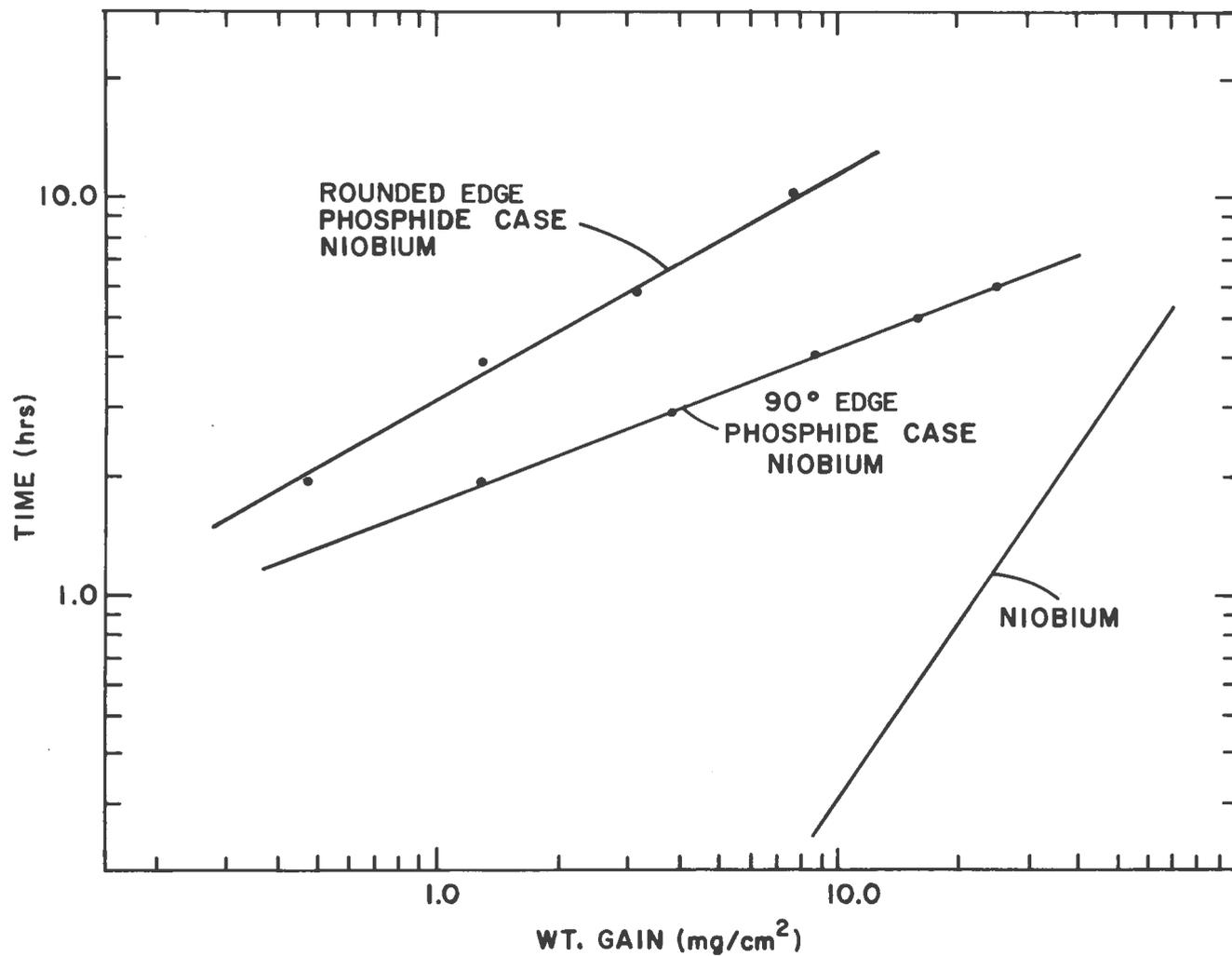


Figure 12. Plots of log of weight gain per unit area against log of time for niobium and average values for niobium phosphide cased samples

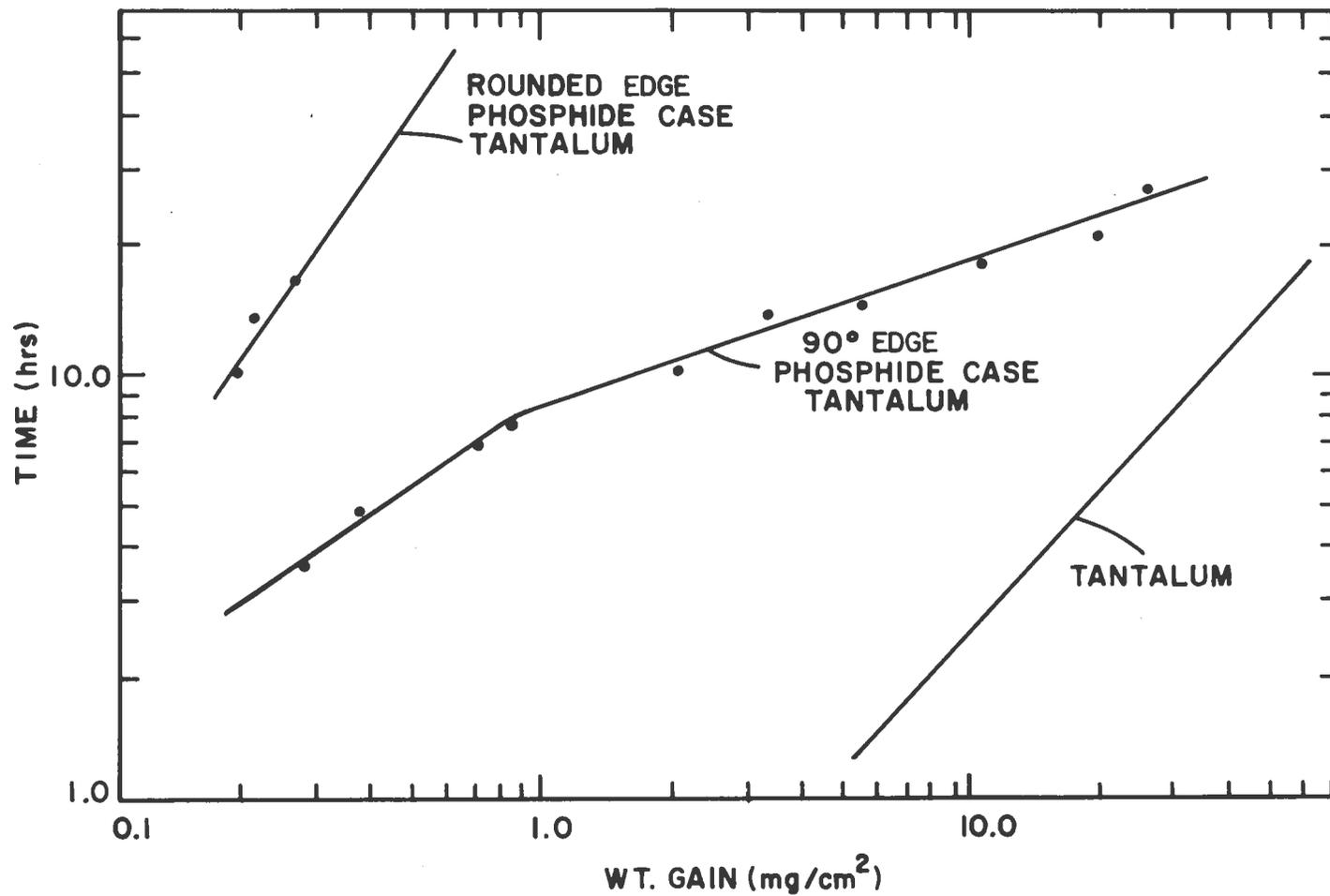


Figure 13. Plots of log of weight gain per unit area against log of time for tantalum and average values for tantalum phosphide cased samples

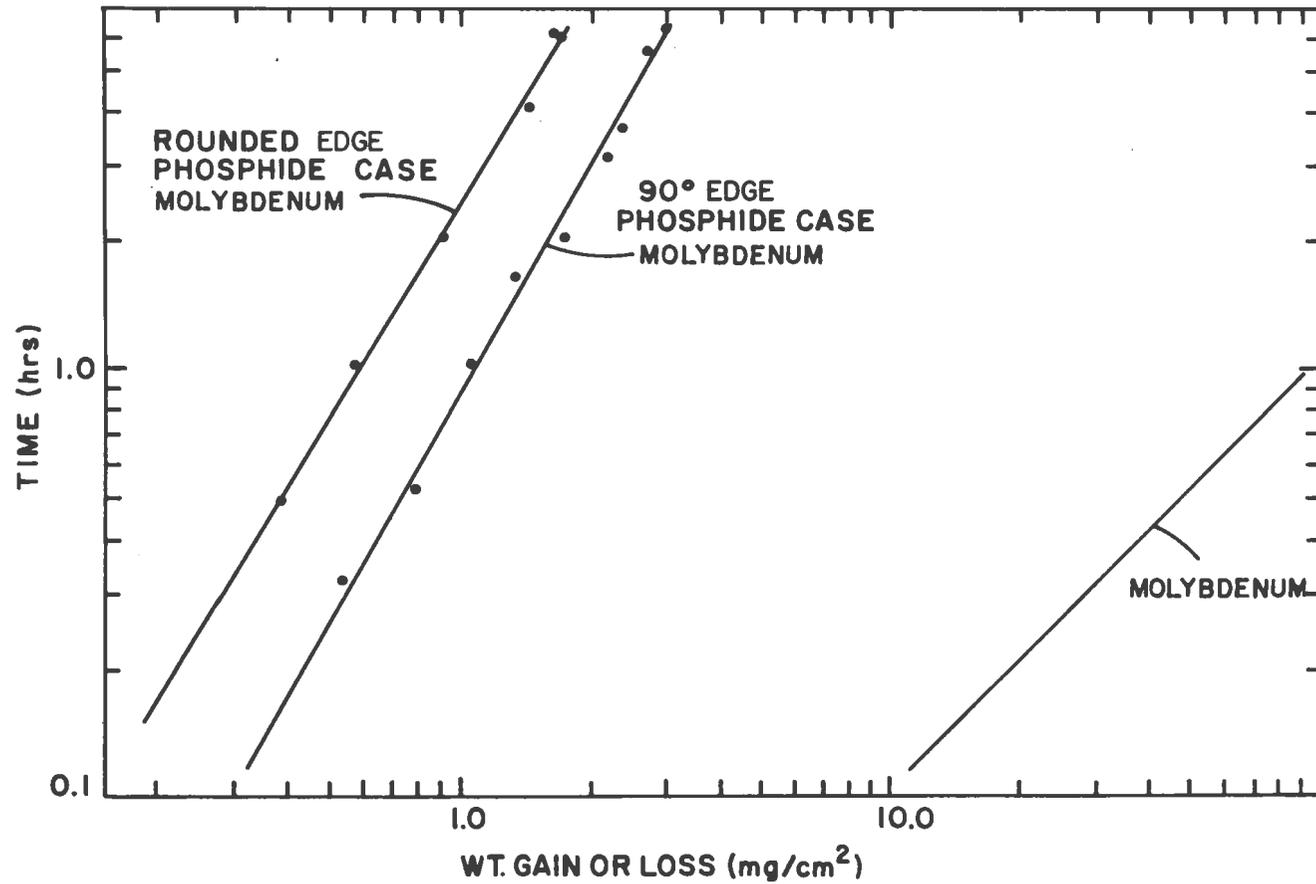


Figure 14. Plots of log of weight gain per unit area against log of time for molybdenum and average values for molybdenum phosphide cased samples

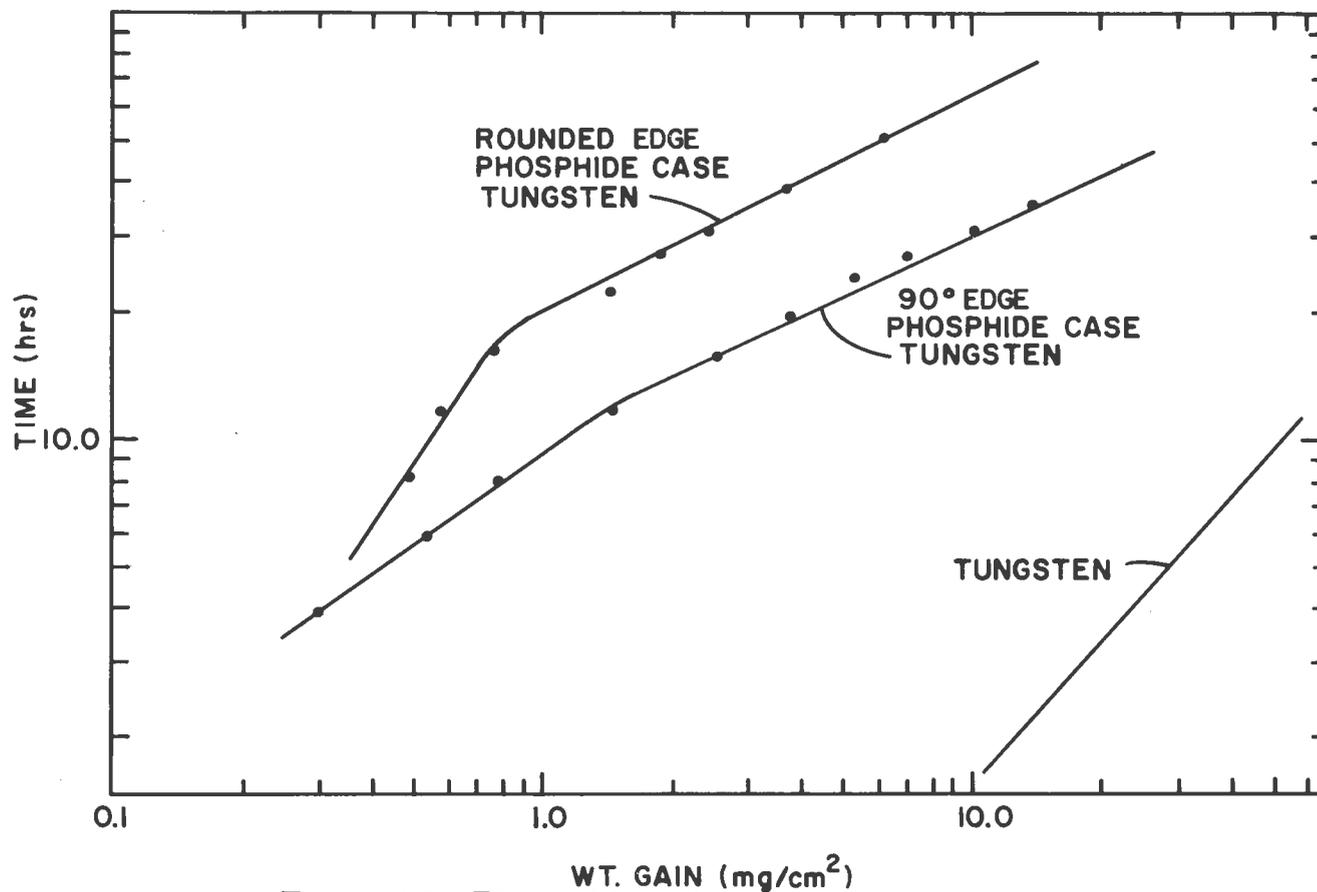


Figure 15. Plots of log of weight gain per unit area against log of time for tungsten and average values for tungsten phosphide cased samples

data were substituted in the previous equation and solved for  $n$ .

The value of  $K$  was determined by substitution of experimental values of  $\Delta m/a$  and corresponding values of  $t$  into the original expression for which  $n$  had been determined. These calculated values of  $n$  and  $K$  that are related to the plots of average weight gain against time are shown in Table 7.

Table 7. Values of  $n$  and  $K$

Material	$n$	$K \frac{g^n}{cm^2 n hrs}$	Time limit
niobium phosphide case, rounded edges	0.578	0.328	limit of test
niobium phosphide case, 90° edges	0.391	0.596	limit of test
tantalum phosphide case, rounded edges	1.19	0.013	limit of test
tantalum phosphide case, 90° edges	0.328 0.511	0.119 0.131	$t < 10$ hours from 10 hours to limit of test
molybdenum phosphide case, rounded edges	1.68	0.406	limit of test
molybdenum phosphide case, 90° edges	1.71	1.16	limit of test
tungsten phosphide case, rounded edges	1.46	0.025	$t < 10$ hours from 10 hours to limit of test
tungsten phosphide case, 90° edges	0.481	0.103	limit of test

The rates at which the metal phosphide cased refractory metals oxidized in all the tests were much less than those of the untreated refractory metals. The weight gain per unit area in all cases was less than 1% of the base metal weight gain for short periods. However the rate of gain for the cased metals increased with time and essentially reached that of the untreated refractory metals after extended time. The length of time required for failure of the phosphided case and thus the advent of rapid weight gain, depended on the refractory metal. The niobium phosphided samples were gaining at the same rate as the substrate after 6 to 7 hours (Figure 8) while tantalum and tungsten were oxidized for 72 and 48 hours respectively before the rate of weight gain was near that of the base material. These points are beyond the time limits of the plots in Figures 9 and 11 respectively. The molybdenum phosphide coated substrates gained weight gradually for 10 to 12 hours (beyond the time limit plotted in Figure 9), then as the coating failed a rapid weight loss was noted. The loss of metal was about one-half of the rate for pure molybdenum and never became more rapid during the oxidation run.

X-ray diffraction patterns were taken of the surface of the oxidized and unoxidized phosphide case specimens by means of a diffractometer. The diffractographs obtained for the specimens were compared. The oxidized and unoxidized phosphide cases for each particular refractory metal showed similarity in their diffractographs inasmuch as the reflection occurred at the same angles of  $2\theta$ . However, in a few cases the reflection intensity ratios for some peaks were not equivalent in

the two samples.

From this x-ray evidence it appears then that the case material on the specimens did not change appreciably during the testing at elevated temperatures.

The cases on phosphided niobium, tantalum and tungsten appeared to fail in the same manner. It would appear that these cases at 800°C give a degree of protection from oxidation by merely retarding the diffusion of oxygen to the base metal. However, the oxide that is slowly formed beneath the case requires a greater volume than the unoxidized metal. The result is a weakening of the case-to-metal bond and eventual rupture of the case, exposing the metal.

The behavior of the phosphide case on molybdenum differed from that of the cases on the other three metals in that the phosphide case on molybdenum appeared to form a viscous liquid film at 800°C when exposed to air. The viscosity of this liquid would decrease with increasing time under these conditions. This liquid would eventually flow sufficiently to leave portions of the base metal exposed to the air. Treatment of samples of phosphide-cased molybdenum by thermal cycling in a muffle furnace had negligible effect on the oxidation resistance of the cases.

The appearance of the metal phosphide-covered substrates before and after oxidation is shown in Figures 16-19.

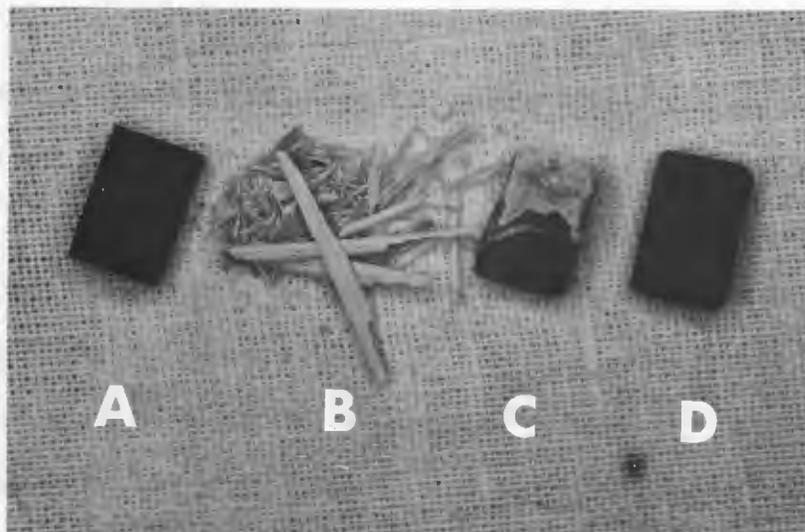


Figure 16. At 1 1/2X magnification: A. Niobium phosphide cased sample in unoxidized condition; B. Niobium oxidized for 3/4 hour; C. Niobium phosphide cased sample with 90° edges, oxidized for 8 hours; D. Niobium phosphide cased sample with rounded edges, oxidized for 8 hours.

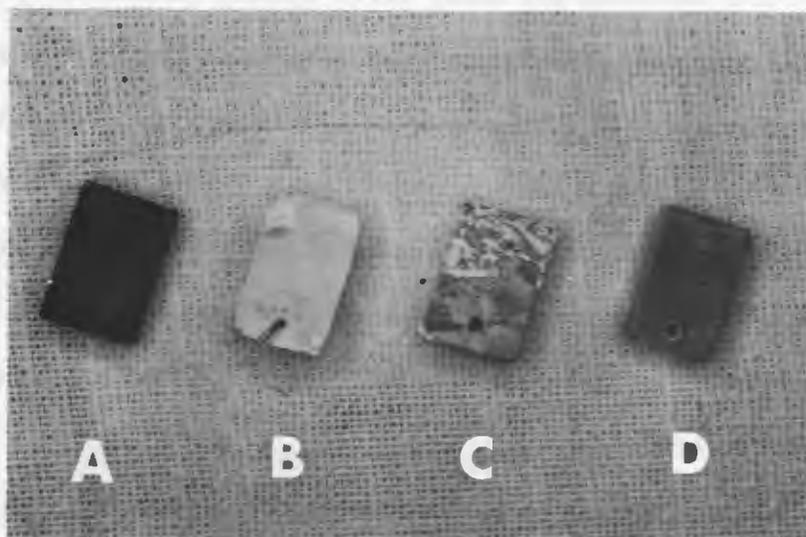


Figure 17. At 1 1/2X magnification: A. Tantalum phosphide cased sample in unoxidized condition; B. Tantalum oxidized for 20 hours (no metal remains, sample is all oxide); C. Tantalum phosphide cased sample with 90° edges, oxidized for 36 hours; D. Tantalum phosphide cased sample with rounded edges, oxidized for 48 hours.

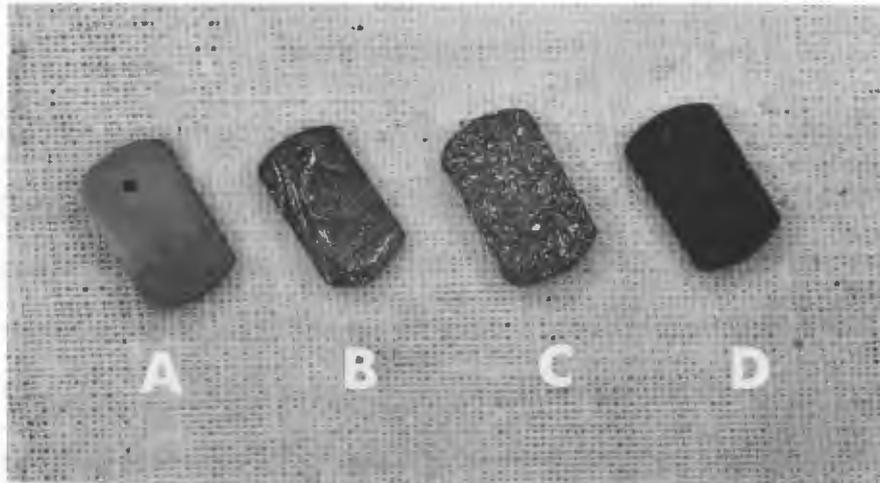


Figure 18. At 1 1/2X magnification: A. Molybdenum phosphide cased sample in unoxidized condition; B. Molybdenum oxidized for 2/3 hour; C. Molybdenum phosphide cased sample with 90° edges, oxidized for 8 hours (viscous coating has flowed from the surface); D. Molybdenum phosphide cased sample with rounded edges, oxidized for 10 hours.

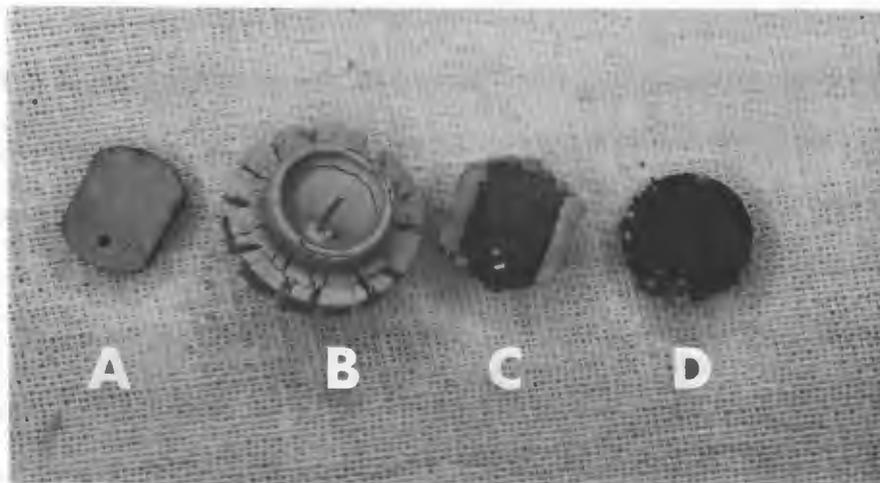


Figure 19. At 1 1/2X magnification: A. Tungsten phosphide cased sample in unoxidized condition; B. Tungsten oxidized for 4 hours; C. Tungsten phosphide cased sample with 90° edges, oxidized for 36 hours (oxide peaks at edges); D. Tungsten phosphide cased sample with rounded edges, oxidized for 72 hours.

## VII. DISCUSSION

Metal phosphide cases on niobium, tantalum, molybdenum and tungsten have a much greater resistance to oxidation than the pure refractory metals. The length of time this resistance is significant at 800°C ranges from several hours to several days depending on the metal, its shape and the case, but if the temperature of service were reduced it is quite possible that the duration of protection would be greatly increased. An increase in time of depressed oxidation probably could be gained by increasing the case thickness.

It can be assumed that a phosphided case and its base metal differ in thermal expansion coefficient. During heating and cooling operations associated with preparation and testing of a sample, stress would then be set up at the case-metal interface with a tendency to promote rupture of the case and reduce resistance to oxidation. No evidence was found for oxidation which could be ascribed to such rupture on flat and smoothly curved surfaces. However, the increased rates of failure at the 90° corners might have been in part attributable to effects of such stresses.

This work points to the desirability of extending the investigation of phosphide cases on these and other metals and their alloys under oxidizing conditions at temperatures above 800°C.

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