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ACKNOWLEDGEMENT

This research was conducted in the laboratories of the Massachusetts Institute of Technology under the direction of Professor Walter C. Schumb, Department of Chemistry, and Professor Michael B. Bever, Department of Metallurgy.

The author wishes to express his sincerest gratitude to Professor Schumb for his inspirational and invaluable guidance and assistance, and for the privilege of working with him.

The author is greatly indebted to Professor Bever for his most estimable assistance in the metallurgical aspects of this work, and for securing the cooperation of his colleagues. In particular, Professors John Wulff, John T. Norton, Herbert H. Uhlig, Albert R. Kaufmann, and Dr. Maria Telkes were very generous in making available facilities for this research.

The gift by Dr. Frank H. Driggs and Dr. L. F. Yntema, Fansteel Metallurgical Corporation, North Chicago, Illinois, of tantalum and molybdenum products for this work, was of great value to the author.

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PART I

I.- Preparation and Analysis of the Alloys

A.- Introduction

B.- Preparation of the Alloys

C.- Preparation of the Alloys for Metallographic  
Analysis

D.- Chemical Analysis of the Alloys



## A. Introduction

The study of the phase diagrams and properties of the high melting metals involves many chemical and metallurgical problems not usually encountered in such number and complexity in the lower melting metals. The high melting metals are found in the heavier members of Groups VA and VIA of the Periodic table, and are characterized further by their reactivity with the common gases and ability to form very stable carbides, as well as by their relative scarcity in the earth's crust. The above factors have retarded the study of the alloy systems of these metals.

In investigating the properties of a binary alloy system of two of these metals, it was advisable to select two metals which together would form a continuous series of solid solutions. The investigation of any other type of system, would have required a complete study of the phase diagram, and would of necessity have restricted the scope of the investigation of the chemical and physical properties. Except for the systems which form a complete series of solid solutions, no complete data are available for the more complicated phase diagrams of the high melting metals.

(1) (2)  
Von Bolton and Bückle reported that tantalum and molybdenum form a continuous series of solid solutions. This system was selected to develop methods of preparation of the alloys and to investigate their corrosion rates and physical properties.

The preparation of the alloys proved to be a major problem. Methods of attaining the high temperatures required were limited when the factor of the reactivity of tantalum and molybdenum with gases and refractories was considered. The high degree of reactivity of tantalum to oxygen, hydrogen, and nitrogen is well known. Tantalum forms carbides readily, and the metal dissolves its own oxide as well as those of other metals present in the common refractories. In many cases, tantalum reduces the refractory oxides, such as alundum. Although molybdenum is not as sensitive to various gases as is tantalum, only those methods which could produce uncontaminated tantalum could be considered, as some methods satisfactory for preparing pure molybdenum would contaminate any alloys containing tantalum. These facts make it mandatory that any method of preparation of tantalum alloys should operate in an

inert atmosphere, such as that provided by the rare gases, or in a vacuum.

(4)

Commercially, tantalum and molybdenum are prepared as powdered metals. The powders are subsequently pressed, sintered, and cold worked. In a more recent method, (5) molybdenum has been prepared in the massive state by fusing a sintered rod in an arc furnace. In his work on tantalum and its alloys, (6) von Bolton prepared small ingots of tantalum by melting the powdered metal in an electric arc furnace.

Thus for the present work, there were available two methods for preparing alloys of these metals; namely, sintering or arc fusion. The sintering technique is accomplished by heating pressed compacts of powdered metals to a temperature near their melting point. The heating is done in vacuum in the case of tantalum. Drastic cold work, followed by further sintering and forging, serve to densify the pure metal and eliminate porosity. The arc fusion method utilizes the heat of the electric arc to melt a pressed compact of the powdered metal. Initial attempts to prepare alloys by pressing and sintering powdered metal compacts of these high melting metals

in a vacuum sintering furnace heated by induction were unsuccessful. The resulting compacts were quite porous, and as no equipment was available to forge or cold work the sintered compacts to densify them, the method had to be abandoned. Bars of metal were also made by electrical resistance sintering of pressed powders; again, the porosity of the resulting pieces made them unacceptable for further work. It was impossible to cold work the bars, as some alloy compositions were very brittle and fractured readily when forged. An attempt was made to hot work the bars by sealing them in an envelope of wrought iron, heating to approximately 1260°C., and swaging the resulting rod. This temperature was insufficient to permit hot working of the tantalum alloy, and the enclosed bar was shattered. As no other material was available to permit the utilization of higher forger temperatures, these alloys were discarded.

(6)  
The arc furnace technique of von Bolton,  
(7)  
modified by Kroll, was next investigated. This method was found to be completely satisfactory for the preparation of sound alloys and was adopted for

the preparation of the alloys studied in this  
research.

## B. Preparation of the Alloys

### 1. Materials Used.

The Fansteel Metallurgical Corporation furnished the tantalum and molybdenum powders used in making the alloys. The tantalum powder, as analyzed by this supplier, contained 0.01% Fe, and 0.03% C, balance Ta; the particle size was minus 80 mesh. The molybdenum powder contained 0.05% oxygen, the balance molybdenum; the particle size was minus 200 mesh. As further purification of the metals was impossible, they were used directly as furnished.

### 2. Pressing

The metal powders were carefully weighed out to give a series of alloys varying from pure molybdenum to pure tantalum, by steps of ten percent. Experience indicated that the arc melting method caused preferential vaporization of the molybdenum, and a very slight excess of the latter was added. The total weight of powdered metals taken was such that a theoretically dense mass of material would give a block,  $\frac{1}{2}$  cubic inches in volume. The powders were placed in 100 cc. ground-glass stoppered jars and tumbled in a mill for 48 hours to insure thorough

mixing. After tumbling, the powders were carefully placed in a cylindrical die, which was fitted with a removable piston and tapered plug. With the base plug in place, the powders were tamped into the die. The piston was then inserted, and a pressure of 50 tons per in.<sup>2</sup> applied in a hydraulic press. After pressing, the compacts, or pressed discs, were stripped from the die. The discs were approximately 1 and 1/8 inches in diameter and 3/8 inches thick. They were quite firm, even in the as-pressed condition. No lubricants were used for the pressing. Hence, there was no contamination, with the exception of some occluded air, and of whatever gases had been previously adsorbed by the powders.

### 3. Sintering

Repeated attempts to melt in the arc furnace green or as-pressed compacts without sintering were unsuccessful, because of the rapid expansion of occluded and/or adsorbed gases when heated suddenly by the arc striking the compact; this expansion caused the compacts to explode. Further, the porosity of the melts obtained in this manner was rather large, whereas melts made of pre-sintered compacts showed little or no porosity. These results indicated the advisability of sintering all ingots prior to melting.

The furnace shown in Fig. 1 was used to presinter the as-pressed compacts. The refractory material was lined on the inner side with several layers of sheet molybdenum, 0.015 inches thick. In turn, several layers of 0.010 inches thick tantalum sheet were placed concentrically inside the molybdenum sheet. In this manner, the compacts were completely isolated from any contact with alundum refractory. The individual ingots were separated from each other by scrap tantalum separators, which had been stamped with raised concentric circles, providing minimum contact between the compact and the separator.

Ten ingots could be charged into the furnace for one pre-sintering operation. The furnace was attached to a mercury diffusion pump of large capacity, and pumped down to 0.1 microns of mercury prior to heating. The system was designed to utilize a high frequency induction unit to heat compacts. The compacts themselves served as the heating element. When the pressure had reached 0.1 microns of mercury or lower, heating was begun. The temperature was determined by a Leeds and Northrup optical pyrometer. When the compacts reached a temperature of approximately 900°C, the pressure rose rapidly as gas was evolved. The pressure then dropped again to 0.1 microns. The heating was continued until a



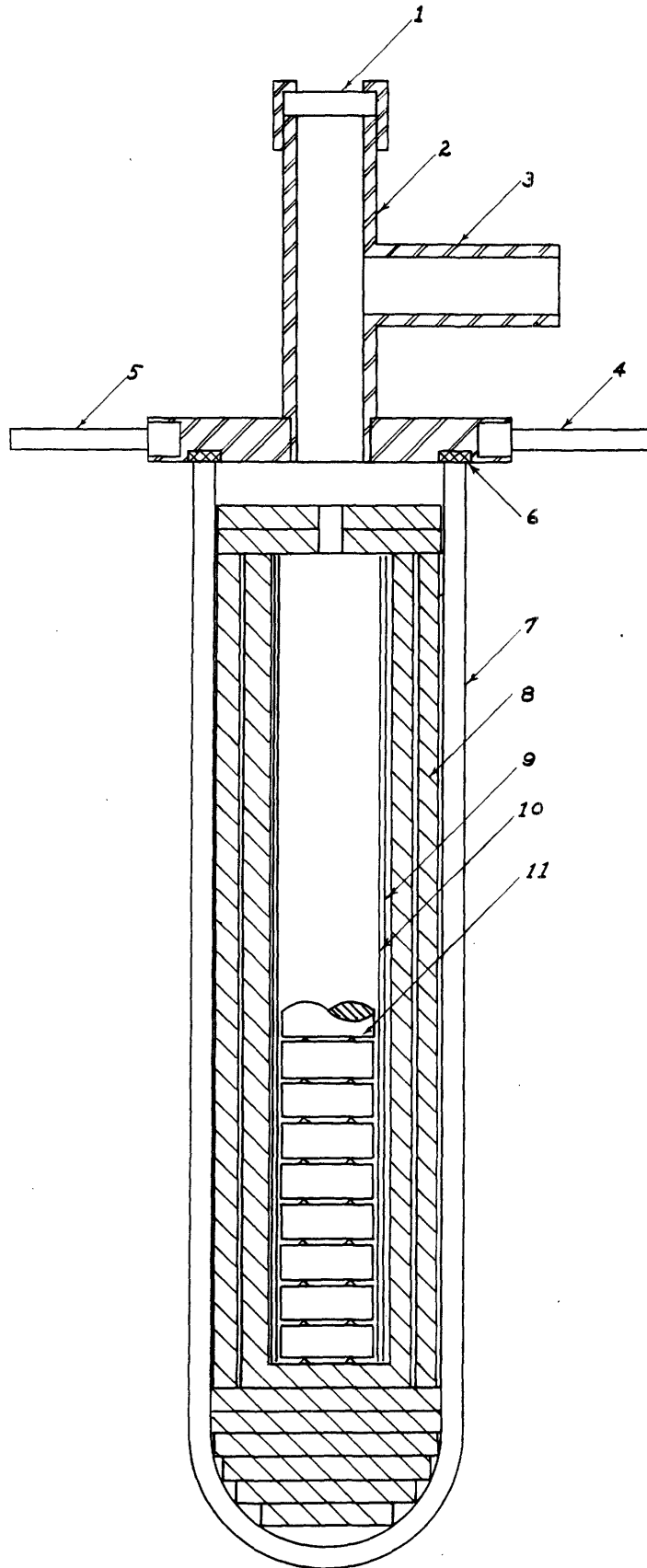
FIGURE 1  
SINTERING AND ANNEALING FURNACE

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- .  
- .  
- .  
- .  
- .  
- .  
- .  
- .  
- .

FIGURE 1

Legend

1. - Vycor sight for optical pyrometry
2. - Brass furnace cover assembly
3. - Outlet to mercury diffusion pump
4. - Cooling water inlet
5. - Cooling water outlet
6. - Silicone rubber gasket
7. - Quartz tube
8. - Alundum liners
9. - Molybdenum reflector
10. - Tantalum reflector
11. - Method of placing compacts or ingots.  
"V" shaped tantalum separators prevent  
contact between individual compacts



temperature of approximately 1600°C was attained; this temperature was held for two hours. The power was then gradually reduced to zero, over a period of approximately two hours. Within eight hours, the charge reached room temperature, and the furnace could be opened.

The sintered compacts shrank from 10 to 15% in volume, their surfaces appeared clean and bright. The points of contact between the compacts and the separators were carefully ground off, and the compacts were ready for melting.

#### 4. Arc Fusion

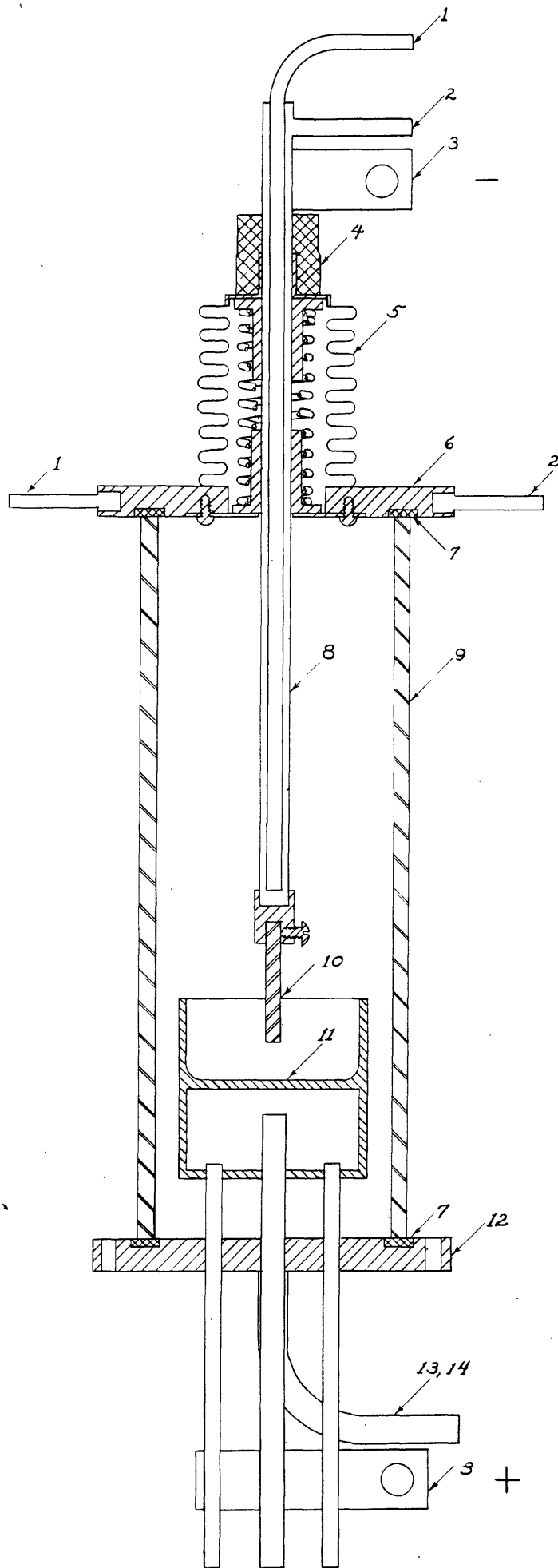
The arc furnace is shown in Fig. 2. It was mounted as part of a complete portable unit. Provision was made for central water cooling and water discharge manifolds to handle the water required to cool the various parts of the furnace. A vacuum pump was provided to evacuate the system for flushing and filling with an inert atmosphere. A gas inlet manifold, complete with bubbler, permitted direct connection of the manifold to a source of argon. Included in this unit, were a series of drying trains to remove traces of moisture, and a heated tub filled with tantalum powder and tantalum foil baffles to remove any residual traces of oxygen and nitrogen which remained in

FIGURE 2  
ARC FURNACE

FIGURE 2

Legend

1. - Cooling water inlet
2. - Cooling water outlet
3. - Terminal lug
4. - Rubber sleeve
5. - Sylphon bellows with spring stiffener
6. - Brass furnace cover plate
7. - Silicone rubber gasket
8. - Movable electrode holder-cathode(negative)
9. - Vycor tube
10. - Tantalum electrode
11. - Water-cooled crucible for supporting compacts during fusion. Serves as anode (positive)
12. - Brass plate for furnace
13. - Two tubes are mounted perpendicularly to the
14. - place of the drawing. One tube serves as inlet for inert atmosphere. The other tube leads to the vacuum pump which serves to evacuate the system.



the argon. The argon, as supplied, was an especially purified grade, 99.96% analyzing argon.

The compact to be melted was placed in the water-cooled copper cup which served as the anode. The system was sealed and evacuated. The system was then slowly filled with argon, again evacuated, and refilled. This cycle was continued three more times to insure the complete removal of all gaseous contaminants. On filling the last time, a pressure of approximately 0.1 atmosphere of argon was established. This pressure gave the best arcing conditions and prevented the development of high pressures in the system when the gas was heated by the arc.

Using an open circuit voltage of 30 to 35 volts, an arc was struck. The closed circuit potential then dropped to 20 to 25 volts, with a direct current of 200 to 400 amperes flowing from the compact to the tantalum electrode. The power was supplied by a heavy duty welding generator. With the current flowing from the specimen which served as the anode to the movable electrode which served as the cathode, the movable electrode did not deposit metal in the melt. On the contrary, metal was deposited on this electrode, and a small gain in weight of the flexible electrode was ob-



served after each run.

The arc was moved over the surface of the compact, completely fusing the mass, with the exception of the underside of the compact. After melting the top surface, the compact was turned over by means of the movable electrode and the bottom portion melted. With practice, smooth, round discs, weighing up to 100 grams, could be made. After fusing, the ingot was allowed to cool to room temperature in the argon atmosphere, and it could then be removed from the furnace. It was a bright, shiny disc, and in many instances, large grains could be seen on the bright surface.

Attempts were made to determine the temperature of the crater in the surface of the specimen as it was being melted. The crater temperature was above the limit of the optical pyrometer used, namely  $3200^{\circ}\text{C}$ . As the temperature gradient between the molten surface and the bottom of the ingot was well over  $3000^{\circ}\text{C}$ , it was necessary to anneal the as-cast ingots to relieve the quenching strains inherent in the ingots prepared by this method.

##### 5. Annealing

The same furnace used for sintering the compacts prior to fusion was employed for annealing the

fused ingots. Each ingot was wrapped in tantalum foil and these packages were stacked vertically in the furnace. The furnace was sealed and pumped down as previously described, and when a pressure of 0.1 microns was obtained, heating by induction was started. The temperature was raised from room temperature to approximately 1600°C in a period of two hours. The ingots were held at this temperature for two hours, then cooled at a rate of 300°C per hour until room temperature was attained. The ingots underwent no change in appearance during the annealing and retained their bright metallic luster.

#### 6. Cutting

The resulting ingots made by melting in the arc furnace were roughly circular in shape, about  $1\frac{1}{4}$  inches in diameter and  $\frac{1}{4}$  inches thick. The surfaces were smooth, but not flat. To obtain bars for corrosion studies and other measurements, the ingots had to be sectioned. The cut-off machine used was equipped with adjustable pressure and feed devices; water jets cooled and lubricated the cutting operation. The irregularly shaped ingots were mounted between lead sheets in a directionally adjustable vise. Rubber bonded alundum cut-off wheels, 8" in diameter and 0.030"

thick were used. The pure molybdenum ingots were sectioned easily; however, the other compositions required from one to one and one-half hours for a single cut through the ingot. The pieces obtained by cutting were ground to rectangular bars on a water-cooled emery belt, using a metal jig to hold the bars in position. The surfaces were finish-ground by hand with No.1 emery paper held on a plate glass surface until all six faces of the bar were plane. The bars were of the order of magnitude of  $3/16$ " x  $1/8$ " in cross section and from  $3/8$ " to 1 and  $1/8$ " long. The dimensions of the brick-shaped bars were measured to 0.0001". The cross section of the bars was an important factor in the determination of several of the properties of the alloys. For this reason great care was exercised in the preparation of the specimens in order to obtain a minimum variation of the cross section over the length of each bar. Within a distance of one centimeter, the variation in the cross section averaged 0.05%.

#### 7. Recovery of the Metals Charged

The powdered metals were mixed so as to produce compositions varying from pure molybdenum to pure tantalum by 10 atomic percent. As the percentage of tantalum increased, the loss of molybdenum due to vaporization in-

creased because of the higher melting temperatures required. Starting with the alloy made up to yield a composition approximating 30 atomic percent tantalum, the amount of molybdenum added was increased by 1% to compensate for these vaporization losses. Table 1 presents the initial composition of the as-pressed compacts and the recovery of the alloys. The composition of the compacts was determined by weighing out and mixing calculated amounts of each powdered metal. The composition of the sintered, arc-fused, and annealed ingots was determined by chemical analysis. The loss of molybdenum by vaporization varied from .1 to 18% of the initial charge of molybdenum.

Table 1

Sample No.	Calculated Composition of the charge as pres- sed compacts		Composition of the ingots after sinter- ing, arc fusion and annealing	
	% Mo	% Ta	% Mo	% Ta
101	100	0	100	0
102	91	10	89.90	10.10
103	81	10	79.92	20.08
104	71	29	69.08	30.02
105	61	39	60.04	39.96
106	51	49	50.53	49.47
107	41	59	38.79	61.21
108	31	69	28.53	71.47
109	21	79	17.23	82.77
110	11	89	8.58	91.42
111	0	100	0	100

C. Preparation of the Alloys for Metallographic Analysis

1. General

The alloys of tantalum and molybdenum, after sectioning, fusing, and annealing, were not difficult to prepare for metallographic examination. The methods suggested in the literature were found to be adequate, although etching of all compositions in this system of alloys requires the use of more than one etchant.

Metallographic examination of the entire range of cast alloys confirmed the conclusions of von Bolton and Bückle that the two elements, tantalum and molybdenum, form a continuous series of solid solutions. The examination further revealed that the method of preparation of the alloys yielded dense, homogeneous ingots. Few, if any, non-metallic inclusions could be found, and only a few ingots showed the presence of pores. In these isolated cases, pores were small and few in number, and were generally located near the surface of the ingot. The pores were spherical in shape, and the inner surfaces were clean and shiny.

Examination of specimens cut from ingots before and after annealing, showed no grain growth. Only in a very few instances in unannealed, as-cast ingots was there any evidence of dendritic segregation. Annealing completely removed these traces of segregation, yielding a homogenized matrix. As annealing did not affect the grain size, the grain size observed in the various compositions was that of the as-cast condition.

## 2. Polishing Technique

Sections were cut from the ingots with a water-cooled and lubricated bonded alundum wheel, described above. They were mounted in bakelite, and rough ground on an emery belt. Regardless of whether the grinding operation was carried out on wet or dry emery belts, only a very light pressure could be applied. Heavy pressure would cause the specimen to be expelled instantly from the mount because of the heat generated, and caution had to be observed during any machine grinding.

The specimens were then ground on emery Paper, starting with No. 1 paper successively thru Nos. 0, 00, and 000, in accordance with standard metallographic technique. (10)

After grinding, the specimens were polished on wheels, using levigated alumina as the polishing medium. Grade No. 1, having the coarsest particle size, was used on a canvas covered wheel, No. 2 on a broadcloth wheel, and No. 3 on a velveteen wheel. It was essential to use very light pressure, slow speed, and to keep the wheel surface well covered with the polishing suspension. Although diamond dust could be used on a special wheel, the aforementioned method was found more satisfactory.

3. Etching Technique (8)(9)

The literature cited recommended for molybdenum an etchant of 10% sodium hydroxide and 30% potassium ferricyanide<sup>(11)</sup> or a solution of 50% nitric acid, followed by washing the specimen with concentrated hydrochloric acid, ammonium hydroxide, and hydrogen peroxide, or a solution of nitric and hydrofluoric acids could also be used for pure molybdenum. Of these, the sodium hydroxide and potassium ferricyanide etchant was found to be most applicable over the greatest range of composition, from pure molybdenum to alloys with a high tantalum content. From pure molybdenum up to and including the alloy containing 50 atomic percent of tantalum



and molybdenum, this etchant was quite satisfactory, although as the amount of tantalum increased, the time and temperature required to etch the specimen increased. Beyond the 50% composition, this etchant was no longer satisfactory.

(9)(12)

Yntema recommends an etchant of one part 48% hydrofluoric acid, one part 95% sulfuric acid, and two parts water; or hydrofluoric acid and ammonium fluoride. It was found that both etchants worked satisfactorily, from pure tantalum to the 50-50 composition. Beyond this composition, the etchant was ineffective.

There is little question that the mechanism of the sodium hydroxide-potassium ferricyanide etchant is one of simple dissolving of the surface metal with preferential attack of the grain boundaries. The molybdenum etchant provides an oxidizing agent and base to form a soluble molybdate. In the case of tantalum, the metal is soluble in hydrofluoric acid forming a soluble fluotantalate. In both of the latter solutions recommended for tantalum, the salt and the acid serve to lower the hydrogen ion or fluoride ion concentration, thereby lowering the activity of the ions concerned in dissolving the metal.

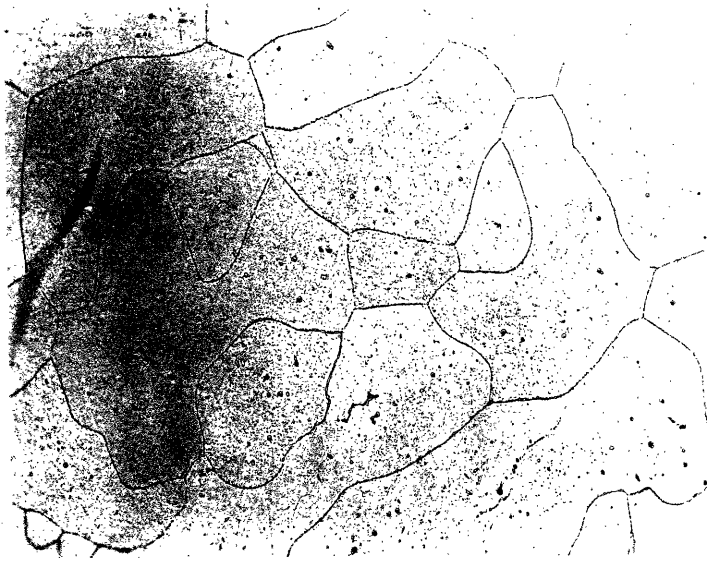
#### 4. Photomicrography

Photomicrographs of specimens of the alloys were taken to record the appearance of the alloys under the microscope. Figure 3 presents photomicrographs of the pure metals and intermediate compositions, before and after annealing, at a magnification of 100X.

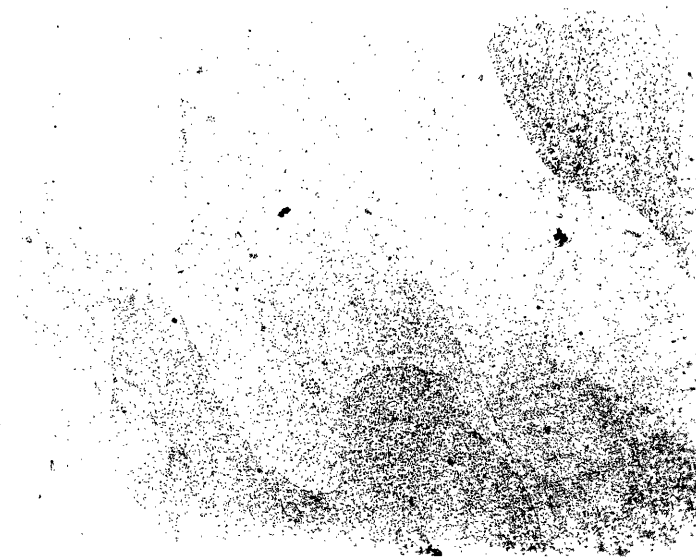
#### 5. Grain Size

The grain size of the cast alloys was determined using the method of Jeffries. <sup>(13)</sup> In Table 2, the grain size is recorded for each composition. The grain size variation was not consistent. The orientation of the long axis of the grains on cooling was perpendicular to the surface cooled. This columnar structure occurs in typical cast structures. Where the grain size was small, there was little preferred orientation. In ingots having large grains, the grains were clearly visible on the surface of the ingot.

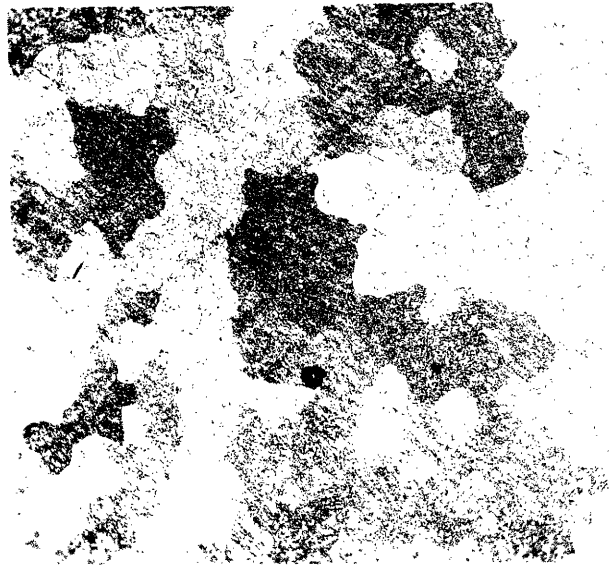
FIGURE 3  
PHOTOMICROGRAPHS OF TYPICAL ALLOYS



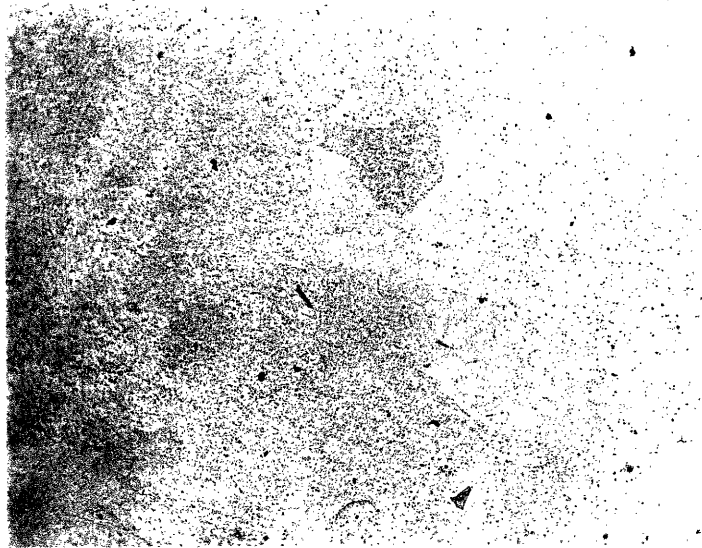
Pure Molybdenum, As Cast



Pure Molybdenum, Annealed



90% Mo, 10% Ta, As Cast



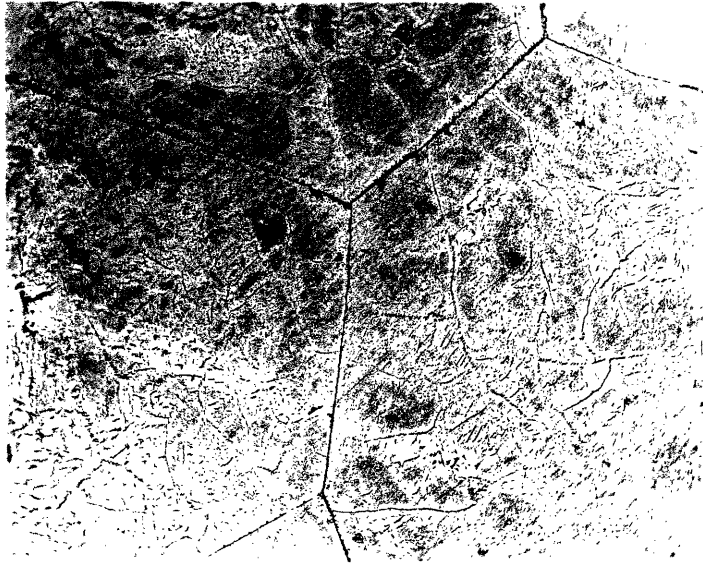
90% Mo, 10% Ta, Annealed



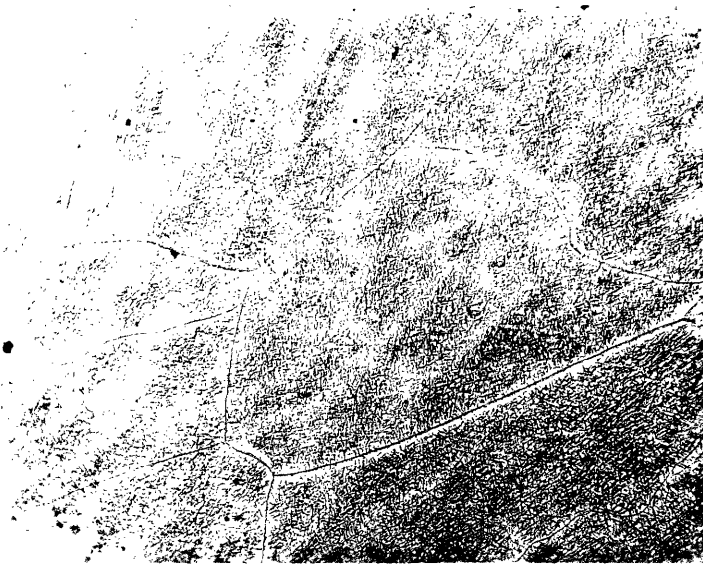
50% Mo, 50% Ta, As Cast



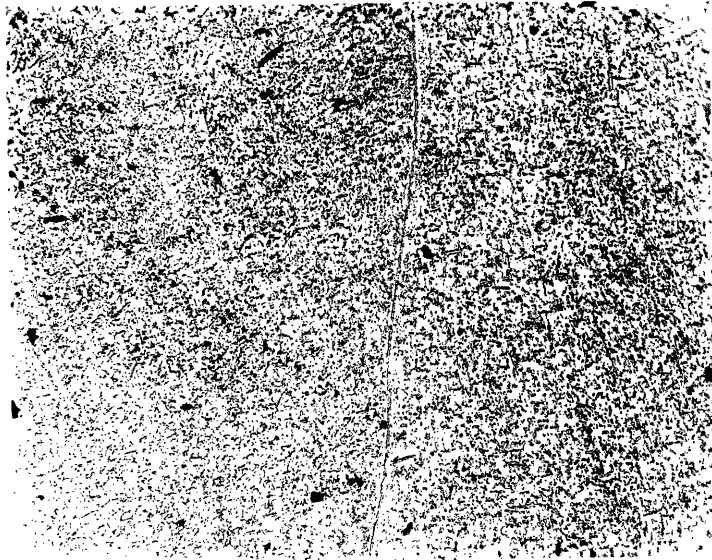
50% Mo, 50% Ta, Annealed



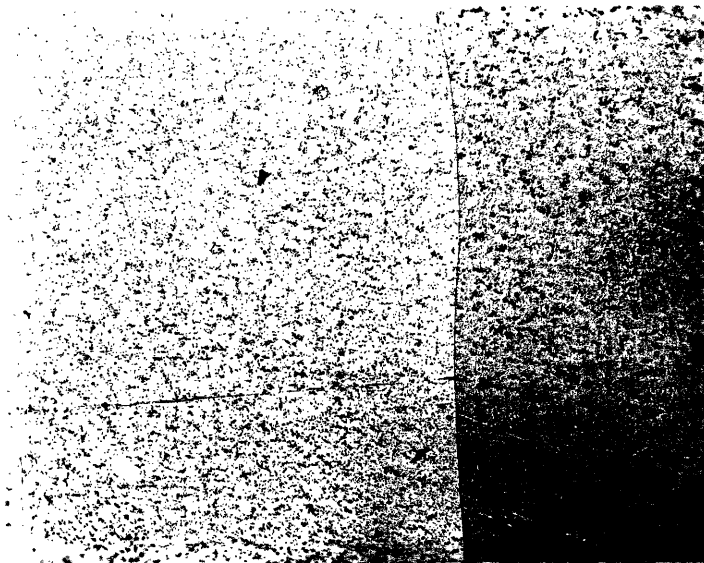
10% Mo, 90% Ta, As Cast



10% Mo, 90% Ta, Annealed



Pure Ta, As Cast



Pure Ta, Annealed



Table 2

## Grain Size of Cast Tantalum-Molybdenum Alloys

<u>Sample No.</u>	<u>% Mo</u>	<u>% Ta</u>	<u>Average Grain Diameter Millimeters</u>
101	100	0	0.123
102	89.90	10.10	0.096
103	79.92	20.08	0.162
104	69.08	30.02	0.146
105	60.04	39.96	0.446
106	50.53	49.47	0.086
107	38.79	61.21	0.133
108	28.53	71.47	0.219
109	17.23	82.77	0.289
110	8.58	91.42	0.333
111	0	100	0.577

D. Analytical Procedure

(14)

As the alloys were composed only of tantalum  
(15)  
and molybdenum, and as the method of preparation  
of the alloys precluded any further contamination,  
it was deemed advisable to analyze for one of the two  
constituents, determining the other by difference.

Various methods were available for analyzing the  
molybdenum by volumetric techniques, but none for  
tantalum. Essentially these methods consisted of  
reducing the molybdenum only to a lower oxidation  
state, then oxidizing the reduced molybdenum to the  
+6 state by permanganate or ceric salts. Zinc re-  
duces the molybdenum to the +3 state, silver to the  
+5 state. As a mixture of hydrofluoric and nitric  
acids was required to dissolve the alloys, these  
methods did not prove satisfactory, inasmuch as  
transient endpoints were encountered because of the  
high fluoride content of the solution and the hydroly-  
sis of the fluotantalates. Hydrous tantalic oxide  
occluded large amounts of molybdenum and rapidly  
clogged the reductor tubes.

(16)

Lundell and Hoffman suggest the separation of  
tantalum and molybdenum by ammonium sulfide, whereby  
advantage is taken of the complete solubility of

molybdenum and complete insolubility of tantalum in solutions of ammonium sulfide. The molybdenum is held in solution as the thio-molybdate and the tantalum precipitates out as the hydrous oxide. This method was investigated in detail and proved to be satisfactory for the analysis of the alloys.

The alloys are readily dissolved in a mixture of hydrofluoric and nitric acids. Samples of from 0.3 to 1.0 grams are used. If the tantalum content is low, the larger weight of sample is used; correspondingly, for a high tantalum content, the smaller sample is recommended.

The sample is placed in a 400 ml. plastic beaker. This may be made readily by cutting off the top of the new type Baker and Adamson 1 lb. hydrofluoric acid bottle, after its contents have been used. It is an efficient and effective container, and many of these vessels were used during the analytical work.

To the sample, 10 ml. of 48% hydrofluoric acid are added. Concentrated nitric acid is then added dropwise very carefully and slowly. The alloy is attacked vigorously with evolution of oxides of

nitrogen. By periodic additions of a few drops of nitric acid, the solution of the metal is readily accomplished. To the concentrated solution, 25 ml. of distilled water are added. This is followed by the very careful addition, dropwise, of concentrated (approximately 15 N) ammonium hydroxide. To prevent spattering, the addition of ammonium hydroxide must be done cautiously. As the solution is neutralized, hydrous tantalic oxide will begin to precipitate out as a white flocculent precipitate. When the solution is neutral, 10 ml. of 15 N ammonium hydroxide and 30 ml. of concentrated ammonium sulfide solution are added. The latter solution was made by chilling a 4 lb. bottle of concentrated ammonium hydroxide to approximately 0°C., then saturating with hydrogen sulfide at 15 lbs/in.<sup>2</sup> The solution of the alloy will turn yellow to a deep bright orange as the molybdate is converted to the thiomolybdate. The color intensity is indicative of the relative concentration of molybdenum. Undoubtedly, a colorimetric determination of molybdenum could be employed, provided blanks were used, as the ammonium sulfide solution may be somewhat colored due to oxidation of the sulfide to polysulfide.

The above solution is digested on a steam bath (not hot plate, because of the plastic beaker), for three to four hours. After the precipitate settles, the supernatant liquid is decanted off, filtering it through S & S No. 589 filter paper, containing a small wad of S & S No. 293 filter pulp in the apex of the cone.

To the precipitate, 50 ml. of a solution made up of 1 part distilled water, 1 part concentrated ammonium hydroxide, and 1 part concentrated ammonium sulfide are added, and the solution is again digested for one to two hours on a steam bath. The filter paper and pulp are washed until white with the ammonium hydroxide-ammonium sulfide wash solution.

The precipitate is washed by decantation five to seven times. The degree of extraction of the molybdenum is indicated readily by the color of the solution above the precipitate. After the precipitate is snow-white, it is washed onto the filter paper with the ammonium hydroxide-ammonium sulfide washing solution, and washed several times thereafter with the washing solution. In washing residues off stirring rods and rubber policemen, distilled water, made basic with ammonium hydroxide should be employed to prevent

peptizing the precipitate on the filter paper.

The precipitate of hydrous tantalic oxide is placed in a porcelain crucible and ignited to constant weight. If the precipitate is dried in an oven prior to ignition, a platinum crucible may be employed.

The method was checked against samples of mixtures of the two pure metal powders containing known amounts of tantalum and molybdenum, and was found accurate to better than 3 parts in 1000. These results are presented in Table 3.

This same accuracy was obtained in routine analyses made of samples ranging from 10 to 90 atomic percent tantalum.

Table 3

## Typical Analyses of Tantalum-Molybdenum Alloys

A. - Analyses of Samples of Known Tantalum and Molybdenum Content  
(Made from mixtures of powders of the pure metals)

	Total wt. of sample	Wt. of Molybdenum	Wt. of Tantalum	Wt. of Ta <sub>2</sub> O <sub>5</sub>	Calculated wt. of Ta from oxide
I	0.9362	0.1388	0.7974	0.9744	0.7979
II	0.9799	0.3086	0.6713	0.8218	0.6730
III	0.3179	0.1924	0.1255	0.1528	0.1252

## B. - Typical Analyses of Cast Tantalum-Molybdenum Alloys

Specimen No.	Wt. of Sample	Wt. Ta <sub>2</sub> O <sub>5</sub>	% Ta. (wt.%)	
103	Sample 1	0.2217	0.0871	32.17
	Sample 2	0.2649	0.1046	32.09
105	Sample 1	0.4054	0.2755	55.65
	Sample 2	0.3293	0.2237	55.63
110	Sample 1	0.3821	0.4446	95.28
	Sample 2	0.5747	0.6682	95.24

## II.- Physical Properties of the Alloys

- A.- Determination of the Density of the Alloys
- B.- Determination of the Hardness of the Alloys
- C.- Determination of the Thermoelectric Power  
of the Tantalum-Molybdenum Alloys
- D.- Determination of the Electrical Resistivity  
of the Tantalum-Molybdenum Alloys
- E.- Determination of the Linear Coefficients of  
Thermal Expansion of the Tantalum-Molybdenum  
Alloys
- F.- Determination of the Magnetic Susceptibility  
of the Tantalum-Molybdenum Alloys



## A. Determination of the Density of the Alloys

The density of the pure metals and alloys was determined by two applications of the principle of Archimedes.

### 1. First Method

#### a. Apparatus

(17) The first method makes use of a pycnometer. The pycnometer consists of a small Erlenmeyer flask with a ground glass neck. A capillary side arm is affixed to the flask bearing a levelling mark and provided with a ground glass cap. The neck of the flask is closed with a ground glass stopper containing a thermometer as an integral part of the stopper. For use in conjunction with the pycnometer, a stock solution of boiled distilled water was prepared. The solution was treated with 0.0004% of Sorbitol, a wetting agent, to insure complete wetting of all internal surfaces in the pycnometer and of the external surfaces of the specimen. The stock solution was well stoppered and maintained at room temperature in the balance room.

The specimens used for the determinations were the bars which had been prepared previously for this research. They were carefully cleaned, washed and

dried, and weighed in air.

b. Experimental Procedure

The specimens were placed in the pycnometer flask. The flask was carefully filled with the stock solution described above by means of an eye dropper in order to prevent the formation of any bubbles. After the flask was filled, the specimen was agitated to remove any adherent gas bubbles. The flask was held in a lintless cloth to prevent heating by the hands of the operator. The stopper was inserted with care and pressed into the neck of the flask with uniform pressure. It was essential to use as nearly as possible the same pressure for insertion of the stopper for all determinations in order to minimize this major source of error in the method - the lack of reproducibility in seating the ground joint. With the aid of a small siphon, the liquid level in the side arm of the flask was carefully lowered to the mark. The temperature of the flask was then recorded, and the flask and contents weighed. The specimen was removed from the flask, and the flask was refilled with the stock solution. The flask filled with water only was weighed at the same temperature as the flask plus the specimen filled with water. After all determinations

were made, the thermometer used in the pycnometer was calibrated with a Bureau of Standards standard thermometer.

## 2. Second Method

The second method applying the Archimedean principle has been described in detail by Fletcher<sup>(18)</sup> and Cohen.

### a. Apparatus

The apparatus for determination of the density by this method is very simple. It consists of a hanger to hold the specimen while it is immersed in the liquid. A fine platinum wire supports a beaker filled with the immersion liquid over the balance pan. In addition to the balance, a calibrated thermometer to record the liquid temperature at the moment of weighing is required. A stock solution of boiled distilled water containing a small amount of wetting agent is utilized as described above as the medium in which the specimen is weighed.

In the determinations made in this research, the hanger consisted of a glass spiral,  $\frac{1}{2}$ " in diameter, with a fine glass V-shaped rod to stiffen the spiral and provide a means of attaching the fine platinum wire. The specimens used were the bars described previously.

b. Experimental Procedure

The weight of the clean, dry bars was determined in air. The weight of the glass hanger and platinum wire with the hanger immersed in the stock solution was determined, and the temperature at the instant of weighing was recorded. Immediately thereafter, the sample was placed in the hanger and immersed in the liquid. The hanger was agitated to remove any adherent bubbles on the hanger or specimen, and the weight of the hanger plus the specimen was determined. It was necessary to remove weights from the weight pan of the balance rather than add weights to it. If the balance arm on the specimen side was low, an error would be introduced as the platinum wire in rising from the surface of the solution would carry with it a film of water on its surface, and this film would be weighed in addition to the hanger and the sample. The temperature was recorded at the instant of weighing.

3. Calculations and Conclusions

The calculation of the density of the alloys by the pycnometer method and by the Archimedean method is very similar. Where variations occur, notation will

be made in the definition of the symbols used:

a = the weight of the specimen in air

b = the weight of the (1) pycnometer filled  
with water alone,  
or

(2) hanger plus sup-  
porting wire weighed  
in the liquid medium.

c = the weight of the (1) specimen in the pycno-  
meter filled with  
water , or

(2) specimen plus the  
hanger and support-  
ing wire weighed in

the liquid medium.

d = the density of the water at the tempera-  
ture at the moment "c" was determined.

The density of the specimen therefore is  
equal to:

$$d = \frac{a \cdot d}{b - c + a}$$

It was found that both of the above methods  
lend themselves to simple and rapid determinations of  
the density of metallic specimens. Both methods checked  
within 0.04% of each other, and there was no systematic

variation in the results observed. The average of the densities of the specimens is presented in Table 4. In Figure 4, the density is plotted as a function of composition, and it may be readily seen that the observed variation of density with composition is nearly a linear function. To three significant figures, the densities observed for the pure metals compare favorably with those reported in the literature. <sup>(8) (9)</sup>

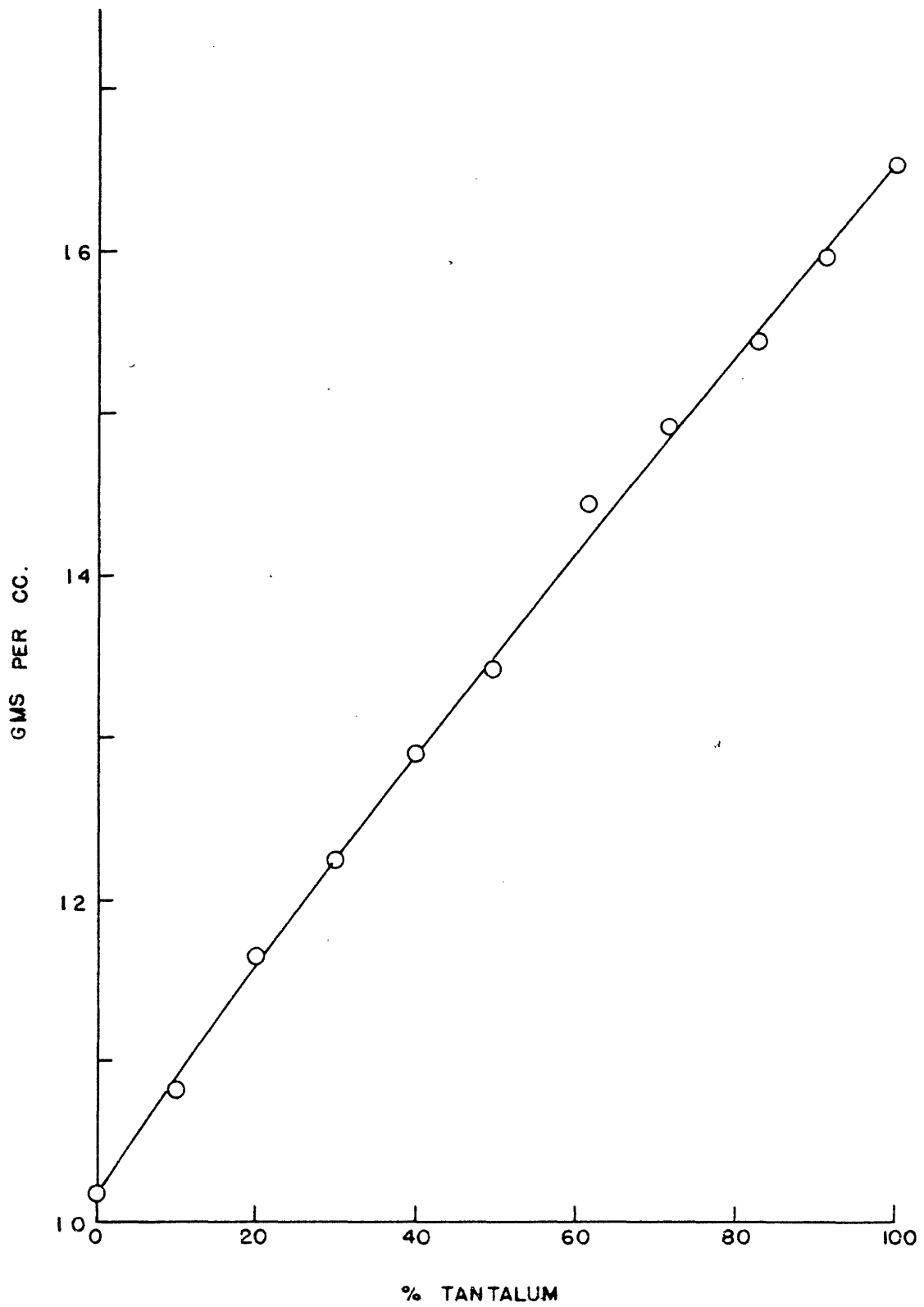
Table 4

## The Densities of the Tantalum-Molybdenum Alloys

<u>Specimen No.</u>	<u>% Mo</u>	<u>% Ta</u>	<u>Density Grams per cubic centimeter</u>
101	100	0	10.16
102	98.90	10.10	10.83
103	79.92	20.08	11.65
104	69.08	30.02	12.25
105	60.04	39.96	12.91
106	50.53	49.47	13.43
107	38.79	61.21	14.47
108	28.53	71.47	14.92
109	17.23	82.77	15.44
110	8.58	91.42	15.96
111	0	100	16.55

FIGURE 4  
THE DENSITY OF TANTALUM-MOLYBDENUM ALLOYS  
AS A FUNCTION OF COMPOSITION





## B. - Determination of the Hardness of the Alloys

### 1. Macrohardness

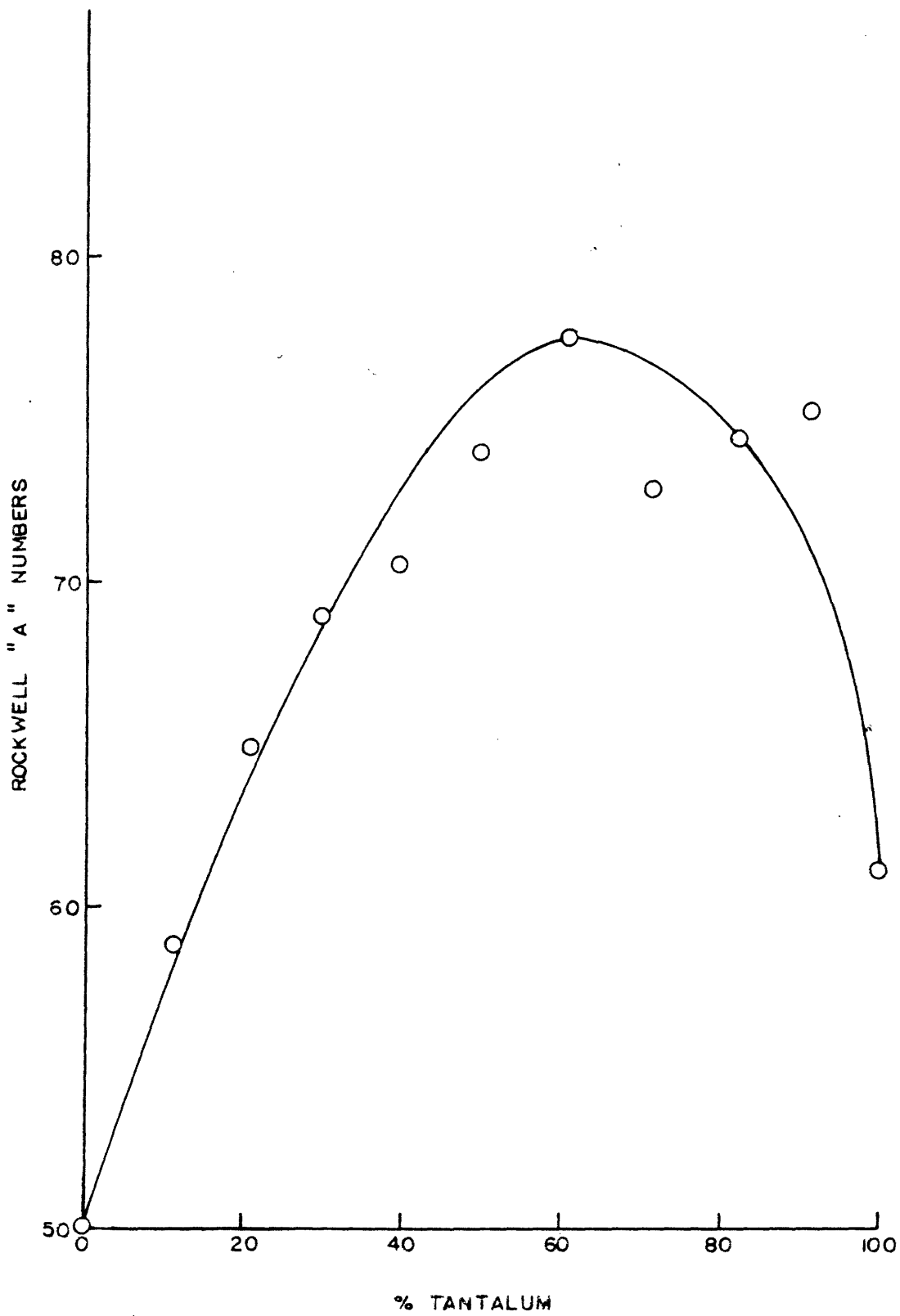
#### a. Apparatus

The macrohardness of the sintered, cast, and annealed alloys was determined by means of a Wilson Rockwell Hardness Tester. As there was a considerable spread in the hardness from pure molybdenum to pure tantalum, it was found advisable to use the Rockwell "A" scale, as this scale covered the entire range in hardness of the series of the alloys. Ingots, from which the bars used in many of the determinations were cut, were used for these determinations. The irregular surfaces were carefully ground flat on both sides of the ingot. Hardness impressions were then made at random over the plane surface. Twelve impressions were made on each specimen, and the average of the twelve impressions for each specimen is presented in Table 5.

#### 2. Observations and Results

The hardness is plotted as a function of composition in Figure 5, and with due allowance made for the effects of grain size on the hardness, it is observed that the variation of hardness with grain size follows the type of curve expected for typical solid solution hardening of two elements when alloyed.

FIGURE 5  
THE MACROHARDNESS OF TANTALUM-MOLYBDENUM  
ALLOYS AS A FUNCTION OF COMPOSITION



C.- Determination of the Thermoelectric Power of Tantalum-Molybdenum Alloys

1.- Apparatus and Experimental Procedure

The thermoelectric power of the alloys was determined in the range of 0 to 100°C. A simple and compact apparatus shown in Figure 7 was utilized for these measurements. It consisted of a copper hot junction and a copper cold junction. The hot junction was heated by steam, and the cold junction was cooled by tap water. The specimen was inserted between the two junctions, and after a steady state was reached, which required from 10 to 15 minutes, the potential across the junction was measured by means of a sensitive potentiometer reading to  $10^{-6}$  volts, and an external galvanometer. In order to measure the temperature differential between the hot and cold junctions, the apparatus included a sensitive thermocouple. A double-throw switch permitted measuring the potential across the hot-cold junction of the specimen or the potential of the thermocouple used to measure the temperature differential between the hot and cold junctions.

The alloy bars discussed previously, were used for determining the thermoelectric power of each alloy. Two determinations for each composition were made. Periodically, a specimen of standard copper was placed

in the apparatus to determine the accuracy of the apparatus. As the potential across a copper-copper junction should be zero, a rapid check could be made.

## 2.- Observations and Results

The potential and temperature differential were recorded. From these data, the thermoelectric power of each alloy composition was calculated by dividing the observed potential by the temperature differential, reporting the thermoelectric power as the micro-volts per degree Centigrade. These data are reported in Table 6, and are the thermoelectric powers of the pure metals and the alloys against copper. These data are plotted in Figure 8. To check the results obtained from the bars having ground surfaces, the thermoelectric power of segments of the cast and annealed ingots from which the bars were cut were determined, and the results were identical. The data for pure tantalum and molybdenum are in agreement with that reported by Potter. In his paper, Potter does not give the previous history of the metal specimens used in his investigation, except that wires of the elements were used.

The results plotted in Figure 8 give a very interesting curve. The precipitous drop at the 50-50 composition was observed in determinations made of two separately cast ingots of the same composition, as well as of the bars cut from the ingots. The entire curve was reproducible from measurements made of bars and of ingots, confirming the unusual curve observed.

FIGURE 7A  
APPARATUS USED FOR THE DETERMINATION OF THE THERMO-  
ELECTRIC POWER OF THE TANTALUM-MOLYBDENUM ALLOYS



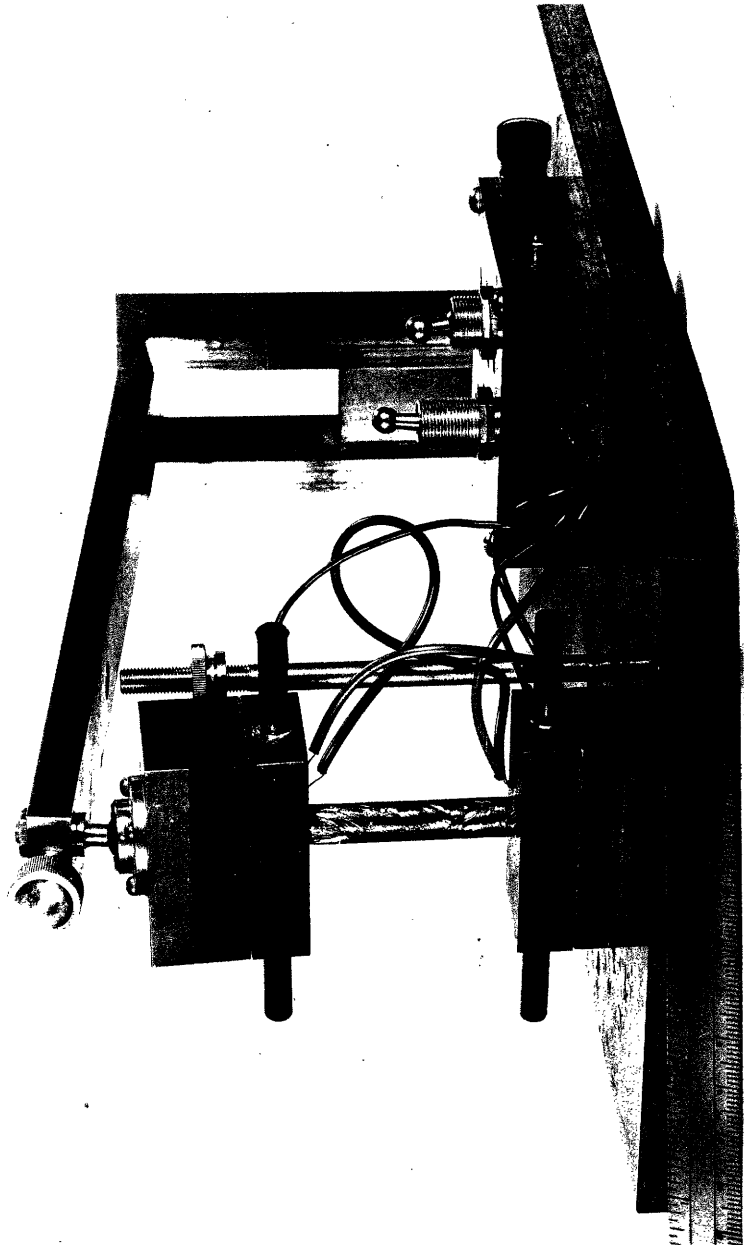


FIGURE 7 B  
SCHEMATIC DIAGRAM OF APPARATUS USED  
FOR THE DETERMINATION OF THE THERMO-  
ELECTRIC POWER OF THE TANTALUM-  
MOLYBDENUM ALLOYS

FIGURE 7 B

Legend

- 1.- Copper block-hot junction
- 2.- Steam Inlet tube
- 3.- Thermocouple leads for measuring temperature differential of the hot and cold junctions
- 4.- Specimen
- 5.- Leads for measuring the thermal potential
- 6.- Cold water inlet tube
- 7.- Copper block-cold junction
- 8.- Selector switch to permit measurement of thermal potential or temperature differential
- 9.- Polarity reversing switch
- 10.- Leads to potentiometer and galvanometer

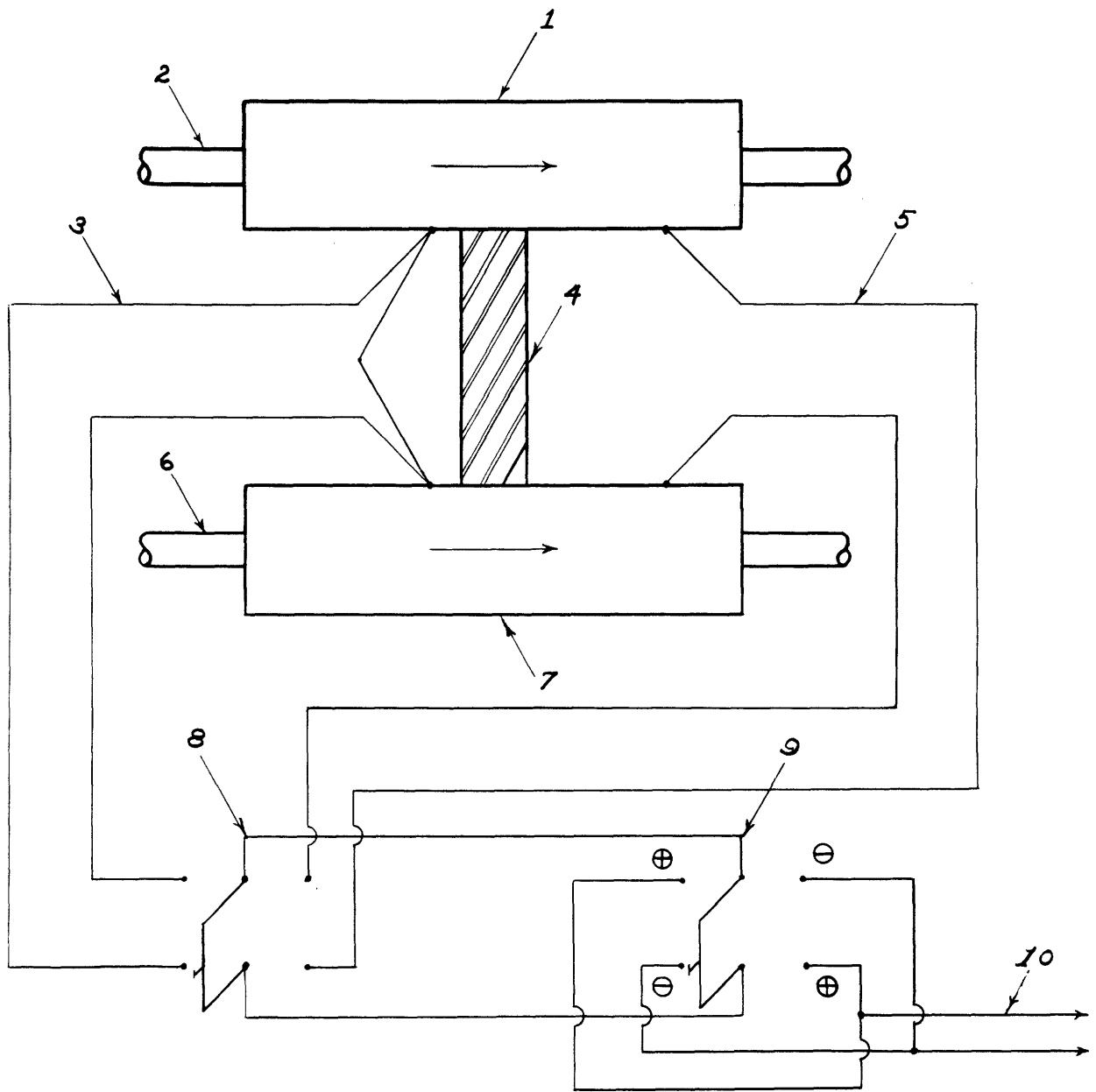
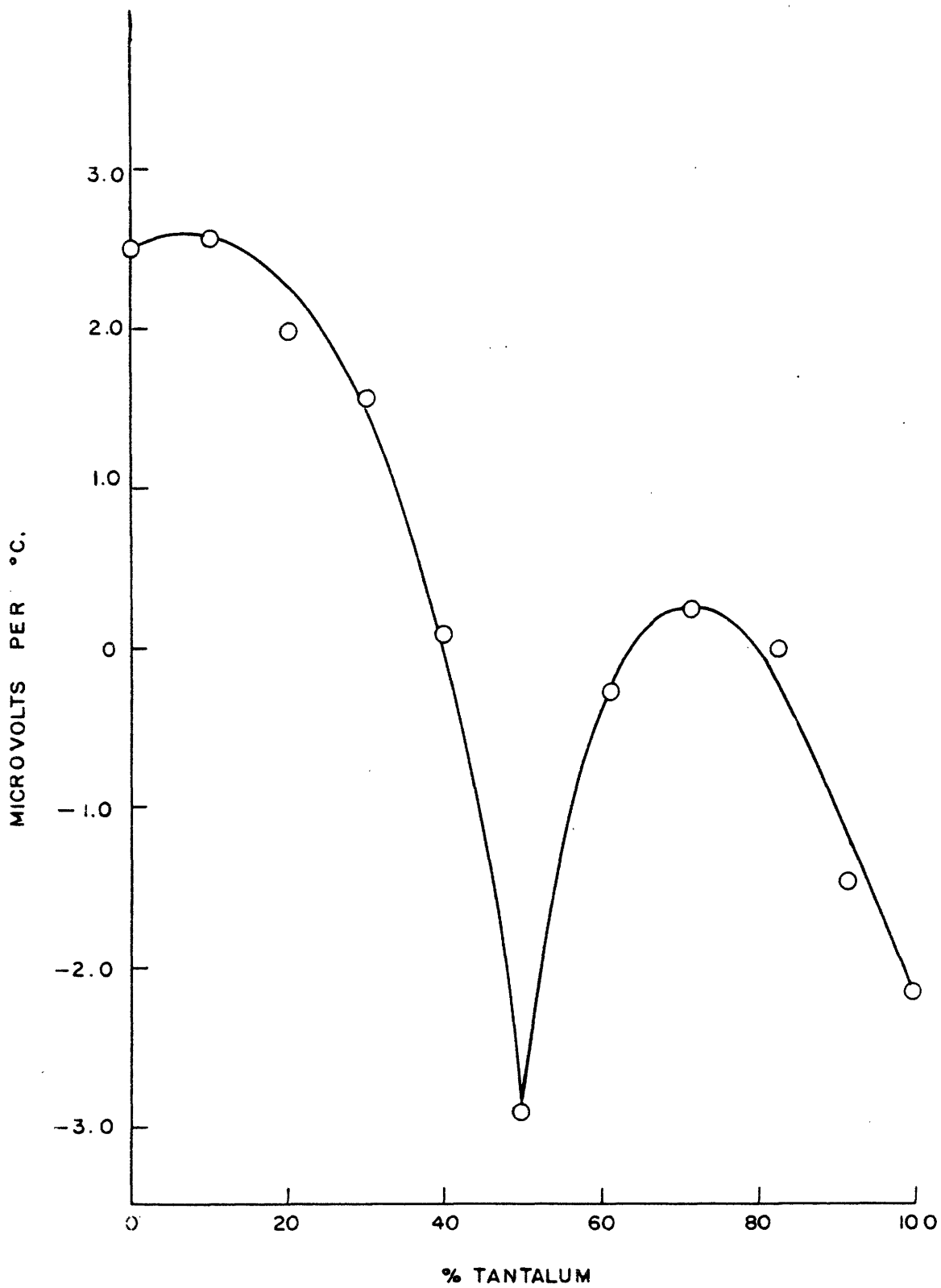


Table 6  
The Thermoelectric Power of the Tantalum-Molybdenum  
Alloys

Specimen No.	% Mo	% Ta	Thermoelectric Power microvolts per °C.
101	100	0	2.51
102	98.90	10.10	2.56
103	79.92	20.08	1.99
104	69.08	30.02	1.59
105	60.04	39.96	-0.09
106	50.53	49.47	-2.90
107	38.79	61.21	-0.28
108	28.53	71.47	0.26
109	17.23	82.77	0.00
110	8.58	91.42	-1.47
111	0	100	-2.15

FIGURE 8  
THE THERMOELECTRIC POWER OF TANTALUM-MOLYB-  
DENUM ALLOYS AS A FUNCTION OF COMPOSITION



D.- The Determination of the Electrical Resistivity of Tantalum-Molybdenum Alloys

1.- Apparatus

The electrical resistivity of the alloy series was determined by means of the apparatus shown in Figure 9. This apparatus was immersed in a constant temperature bath filled with a petroleum base oil. The oil bath could be heated by means of a steam coil with an auxiliary bayonet-type heater connected in series with a thermostat to bring the bath up to the desired temperature.

The apparatus was connected in series with a battery, variable resistance, and ammeter which permitted the passage of a variable current the amperage of which could be measured directly. Two contacts, of known separation, could be applied to the surface of the specimen whose resistance was being measured. The contacts were connected to a sensitive potentiometer and external galvanometer previously described.

2.- Specimens Used

The method by which specimens were prepared in the shape of bars was described in Section I. These bars were used for the determination of the electrical resistivity. They were prepared with plane faces, and with a nearly constant cross section over the length of the bar. Over a



distance of one centimeter, the cross section of each bar did not vary more than 0.05%.

### 3.- Experimental Procedure

For each determination, it was necessary to know the mean crosssection of the bar, the temperature at which the determination was made, the potential contact separation, the potential across the electrode separation, and the amperage. In order to determine the specific resistance of the alloys at room temperature, each bar was placed between the adjustable contacts of the apparatus and clamped in place. The two contacts were clamped against the bar, and were located so that they were equidistant from the midpoint of the bar. The apparatus was then placed in the constant temperature bath and allowed to come to equilibrium. The temperature of the bath was then measured with a standard Bureau of Standards thermometer. As a current of known amperage was passed through the bar, the potential across the known separation of the potential contacts was measured.

A second set of determinations was made in exactly the same manner at a temperature near 100°C. Knowing the specific resistance at two different temperatures, it was possible to determine the thermal coefficient of electrical resistivity.

#### 4.- Results Observed

The data for the electrical resistivity at 20°C. and the coefficient of electrical resistivity are presented in Table 7.

FIGURE 9  
APPARATUS FOR THE DETERMINATION OF THE  
ELECTRICAL RESISTIVITY

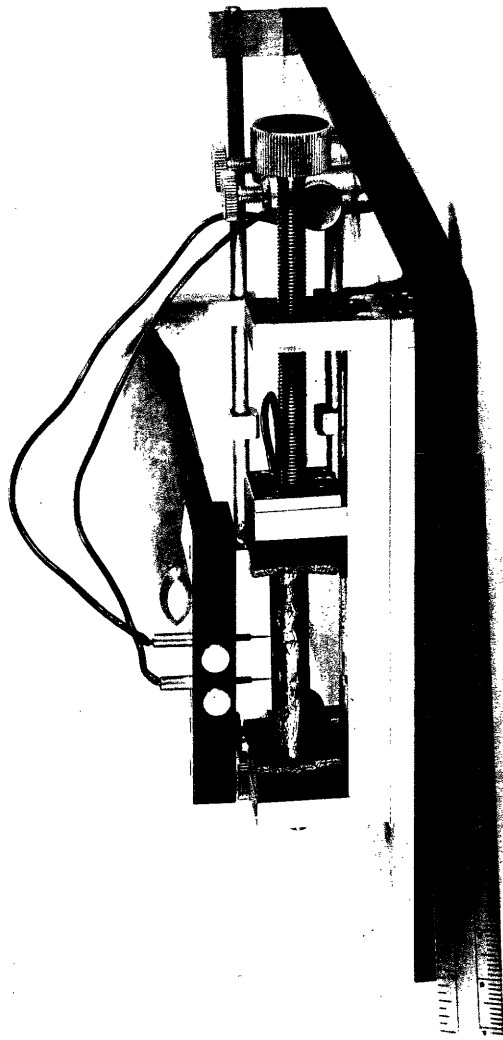


Table 7  
The Electrical Resistivity of Tantalum-Molybdenum  
Alloys

Specimen No.	% Mo	% Ta	Specific Re- sistance micro- ohm-cms 20°C	Thermal Coefficient of Electrical Resistivity 20°C-100°C. 10 <sup>-3</sup>
101	100	0	5.72	-6.53
102	89.90	10.10	9.89	-2.31
103	79.92	20.08	13.23	-4.23
104	69.08	30.02	17.32	-3.94
105	60.04	39.96	20.83	-3.93
106	50.53	49.47	25.10	-1.06
107	38.79	61.21	45.90	3.48
108	28.53	71.47	35.90	0.17
109	17.23	82.77	31.62	-0.0093
110	8.58	91.42	26.60	0.61
111	0	100	25.82	0.363

E.- Determination of the Linear Coefficients of Thermal Expansion of Tantalum-Molybdenum Alloys

1. Apparatus

The apparatus shown in Figure 11 was employed in the determination of the coefficients of thermal expansion of the tantalum-molybdenum alloys. The apparatus consisted of an electrical resistance furnace equipped with a variable resistance for control of the heating rate. A Vycor tube with an asbestos cap was employed to support an inner quartz tube which held the specimen being studied. The Vycor tube also served as a jacket to prevent oxidation of the specimen during the determination. A small Vycor tube entered the cover and extended down to the point of support of the specimen. Through this latter tube, dried, 99.96% argon was bled in constantly to provide an inert atmosphere. The inner quartz tube contained a second hollow quartz tube which rested on top of the specimen and extended up through the outer quartz tube. The inner quartz tube contained a chromel-alumel thermocouple for measurement of the temperature of the specimen. A very sensitive penetration gage, measuring to 0.0001" was placed in contact with the inner quartz tube, and rested directly on the inner tube. An electrical buzzer was mounted on the gage support to permit gentle vibration of the system to

eliminate the lag in measurement of the expansion.

## 2.- Experimental Procedure

The bars previously described were measured with a micrometer gage to 0.0001". Each bar was placed in the outer quartz support and the inner quartz tube placed on top of the bar. The tubes were placed in the Vycor tube, covered, and the gage was placed on the inner quartz tube and set at zero. The system was flushed with argon, and heating was started at a rate of 2.5°C. per minute. The temperature and gage reading were measured at three minute intervals during the period in which the specimen was heated to 650°C.

To calibrate the instrument and check the observations made, a specimen of nickel, analyzing 99.36% nickel, was placed in the apparatus and its expansion measured. As the coefficient of thermal expansion of nickel is well known, it was possible to calibrate the apparatus, and adjust the observed results for the tantalum-molybdenum alloys accordingly.

### 3.- Observations

In all cases, plotting the linear expansion as a function of the observed temperature over the range of room temperature to 650°C., showed that the relationship of linear expansion to temperature was linear. The observed linear coefficients of thermal expansion are presented in Table 8.

The linear coefficient for pure molybdenum was observed as  $5.87 \times 10^{-6}$  over a range of 20°C to 650°C., whereas over a range of 20°C to 100°C., the linear coefficient has been reported as  $4.9 \times 10^{-6}/^{\circ}\text{C.}$  <sup>(8)</sup> For pure tantalum, the observed value over the range of 20°C to 650°C. was  $5.64 \times 10^{-6}/^{\circ}\text{C.}$  The reported value for the linear coefficient of pure tantalum over the range of 20°C to 100°C. is  $6.5 \times 10^{-6}/^{\circ}\text{C.}$  <sup>(9)</sup>



FIGURE 11  
DILATOMETRIC APPARATUS FOR DETERMINING THE LINEAR  
COEFFICIENT OF THERMAL EXPANSION

FIGURE 11

Legend

- 1.- Dilatometer Gage
- 2.- Thermocouple leads, (chromel-alumel couple)
- 3.- Thumbscrew for height adjustment
- 4.- Electric buzzer
- 5.- Stand for supporting gage and quartz apparatus
- 6.- Quartz outer tube for supporting specimen. Quartz inner tube for transmitting thrust from expansion of specimen to the gage
- 7.- Asbestos Cap
- 8.- Gas delivery tube for providing argon atmosphere to system
- 9.- Ring support for outer Vycor tube
- 10.- Furnace
- 11.- Outer Vycor tube
- 12.- Specimen seated in quartz saddles in thrust and support tubes. Thermocouple junction in contact with specimen
- 13.- Quartz saddle

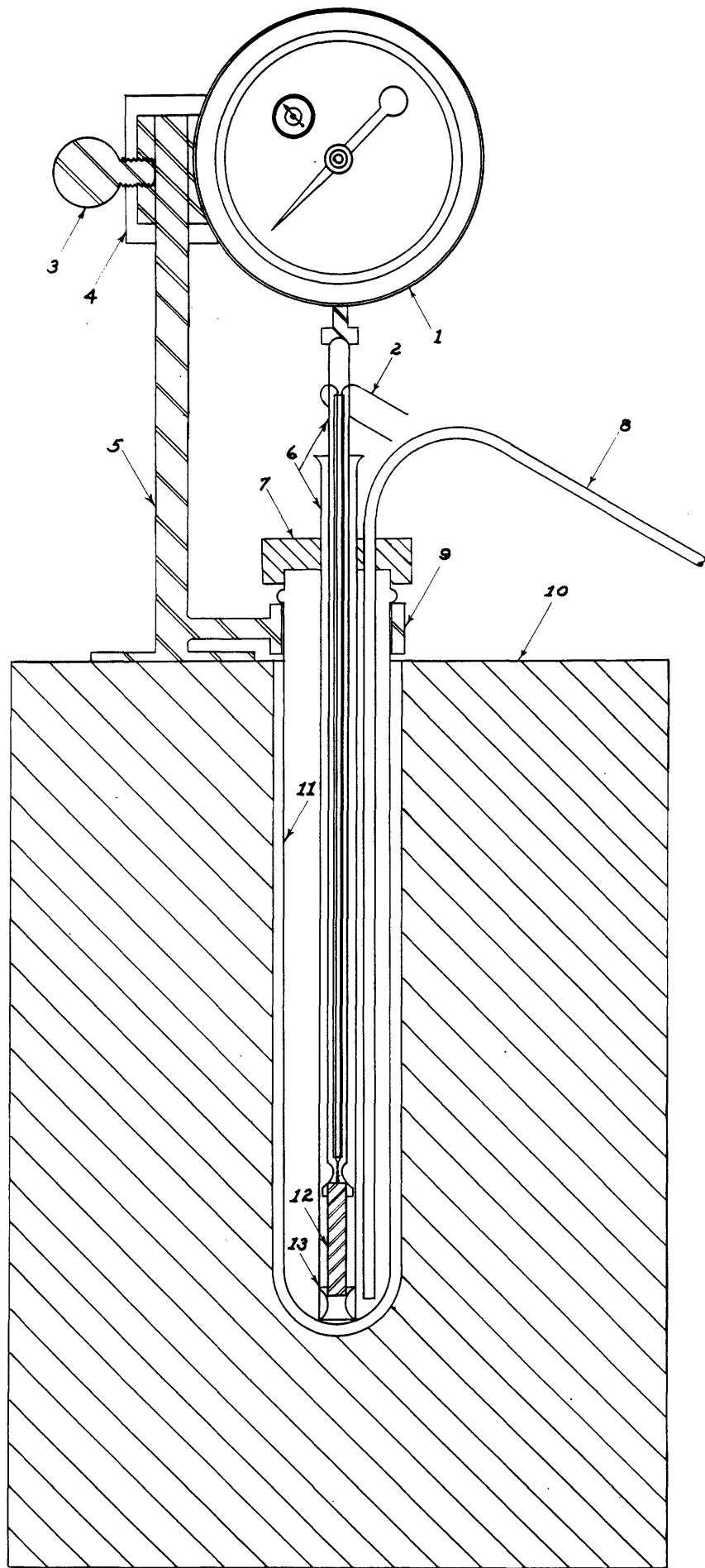


Table 8

The Linear Coefficients of Thermal Expansion of  
Tantalum-Molybdenum Alloys. (20°C to 650°C)

Specimen No.	% Mo	% Ta	Linear Coef- ficient of Thermal expansion $10^{-6}/^{\circ}\text{C}$
101	100	0	5.87
102	89.90	10.10	6.51
103	79.92	20.08	5.15
104	69.08	30.02	4.89
105	60.04	39.96	6.91
106	50.53	49.47	7.59
107	38.79	61.21	7.91
108	28.53	71.47	6.00
109	17.23	82.77	5.27
110	8.58	91.42	2.96
111	0	100	5.64

F.- Determination of the Magnetic Susceptibility  
of Tantalum-Molybdenum Alloys

In the investigation of the physical properties of the tantalum-molybdenum alloys, it has been planned throughout to determine their magnetic susceptibilities. Equipment required for this work has been unavailable, and will not be available until June. At that time, the author plans to carry out this experimental work, and the results will be added to this paper.

III.- Corrosion of the Alloys in Concentrated  
Acids

A.- Apparatus

B.- Specimens Employed

C.- Corrosion Rate of Tantalum-Molybdenum Alloys  
in Concentrated Sulfuric Acid

D.- Corrosion Rate of Tantalum-Molybdenum Alloys  
in Concentrated Hydrochloric Acid

E.- Corrosion Rate of Tantalum-Molybdenum Alloys  
in Concentrated Nitric Acid

### III.- Corrosion of the Alloys in Concentrated Acids

#### A.- Apparatus

In designing apparatus for studying the corrosion of metals, the various factors affecting the rate of corrosion must be controlled, and the apparatus used must provide these controls. Such factors as temperature, atmosphere in the system, concentration of the corroding medium, rate of agitation of the corroding solution and the acid employed have a pronounced effect on the rate of corrosion. In addition, the method of supporting the specimen and the angle at which it is supported can affect the rate, and must therefore be controlled, or held uniform for all corrosion runs.

In Figure 15, a schematic diagram is presented. The constant temperature bath was of large heat capacity and thermal stability. Two immersion heaters operated constantly to keep the bath near the desired temperature, and a third heater, operated by a sensitive thermostat, maintained the bath at the desired temperature. The variation in temperature in the bath, checked continuously over a period of several

days, was  $\pm 0.08^{\circ}\text{C}$ . For all corrosion runs, the bath was held at a temperature of  $55^{\circ}\text{C}$ . As the evaporation rate of the water bath was quite high, it was necessary to provide make-up water. A float type levelling device connected to the cooling water supply permitted the continuous addition of make-up water without disturbing the temperature of the system. The temperature variation above was measured during the continuous addition of water by the levelling device.

As molybdenum is moderately resistant to corrosion in acids, and tantalum is exceedingly resistant, it was desirable to determine the corrosion rate under the most corrosive action possible. Oxygen was therefore used as the atmosphere, and all runs were carried out with the medium and the atmosphere saturated with oxygen at one atmosphere pressure. In addition to providing the atmosphere for the corrosion runs, the gas was used to agitate the corroding solution. A bubbler was located in the center of each corrosion jar, and a glass chimney was affixed to the bubbler column to direct the stream of bubbles in a vertical direction. The bubbles in rising through the



chimney caused the solution to move upward through the chimney, then downward over the metal specimens which were hung radially around the chimney. The specimens were supplied continuously with fresh oxygen-saturated solution. A flowmeter was installed in the gas feed line, in order that all corrosion jars could be stirred at the same rate. The oxygen was bubbled into the jars at a rate of 200 cubic centimeters of oxygen at one atmosphere per minute.

All corrosion runs were carried out with concentrated acids - sulfuric, hydrochloric, and nitric acids. In order to prevent loss of the volatile acids, the gas entering the system was saturated with the acid used in the run by means of a saturator filled with the particular acid being employed. Above each corrosion jar (see Figure 14) a water cooled column condenser was installed. The gas feed line passed down through the center of the condenser column, thereby reducing the internal volume of the condenser column and insuring greater contact between the effluent gas and the cooling surface of the column. The discharge water from the condensers was fed directly to a large tank in which the gas saturator was located. By this means, the gas entering

the system was saturated with the corroding medium at the same temperature at which the gas left the system. In order to prevent air from entering the system, a trap was built into the discharge side of the condenser. The corrosion jars were of large capacity, holding 6.5 liters of solution. It was determined that if all samples in each jar corroded completely, the concentration of the acid would be reduced by approximately 0.1% of its original normality. It can be seen, therefore, that the acid concentration would vary only inappreciably, because of the solution of the samples. In addition, the corrosion jars were covered with plates, ground to fit the jars used. A silicone grease seal was used, and it was demonstrated by preliminary experiments that this grease remained only on the cover plate, and did not enter the corroding medium. However, because of the gas flow through the solution, there was a tendency for a slight amount of the acid to be carried out of the system. This loss of acid occurred only with hydrochloric and nitric acids, and the decrease in concentration was very small.

The acids studied were the more common ones—sulfuric, hydrochloric, and nitric acids. They were used in the concentrations in which they are supplied;

namely, 95.5% C. P. sulfuric acid, 37% C. P. hydrochloric acid, and 70% C. P. nitric acid.

The specimens were mounted in Pyrex glass spirals,  $\frac{1}{2}$ " in diameter, made of fine Pyrex rod, approximately 0.5 mm in diameter. An exploded view in Figure 14 portrays the hangers used and illustrates the method of placing the specimens in the hangers and the angle at which the specimens were held in the hangers. This type of hanger permitted minimum contact between the specimen and the support, as the specimen touched the support only at its corners and contact was tangential to the curved surface of the Pyrex rod, of which the spiral type hanger was constructed. The specimens were placed in the hanger so that the large plane surfaces were at an angle of  $45^\circ$  to the vertical.

#### B.- Specimens Employed

An important factor in the rate of corrosion is the previous history of the metal being studied. The previous history must include the method of preparation of the metal, the treatment it has received, that is whether the metal had been cold worked, hot worked, or whether it was in the annealed state. The surface condition must be uniform for all specimens studied, and it is imperative that the surfaces be clean and

FIGURE 14  
CORROSION JAR

FIGURE 14

Legend

1. - Gas inlet tube
2. - Stopper
3. - Cooling water outlet
4. - Water-cooled condenser
5. - Gas outlet air trap
6. - Cooling water inlet
7. - Tygon sleeve gasket
8. - Hook for hanging corrosion specimen hangers
9. - Glass cover plate
10. - Ground glass surfaces on jar and cover plate
11. - Liquid level in constant temperature bath and corrosion jar
12. - Pyrex jar
13. - Chimney to control internal liquid currents in corrosion jar
14. - Fritted glass bubbler
15. - Enlarged view of corrosion specimen hanger showing method of placing specimens. The hanger is supported in the corroding medium by the hanger hooks (8)

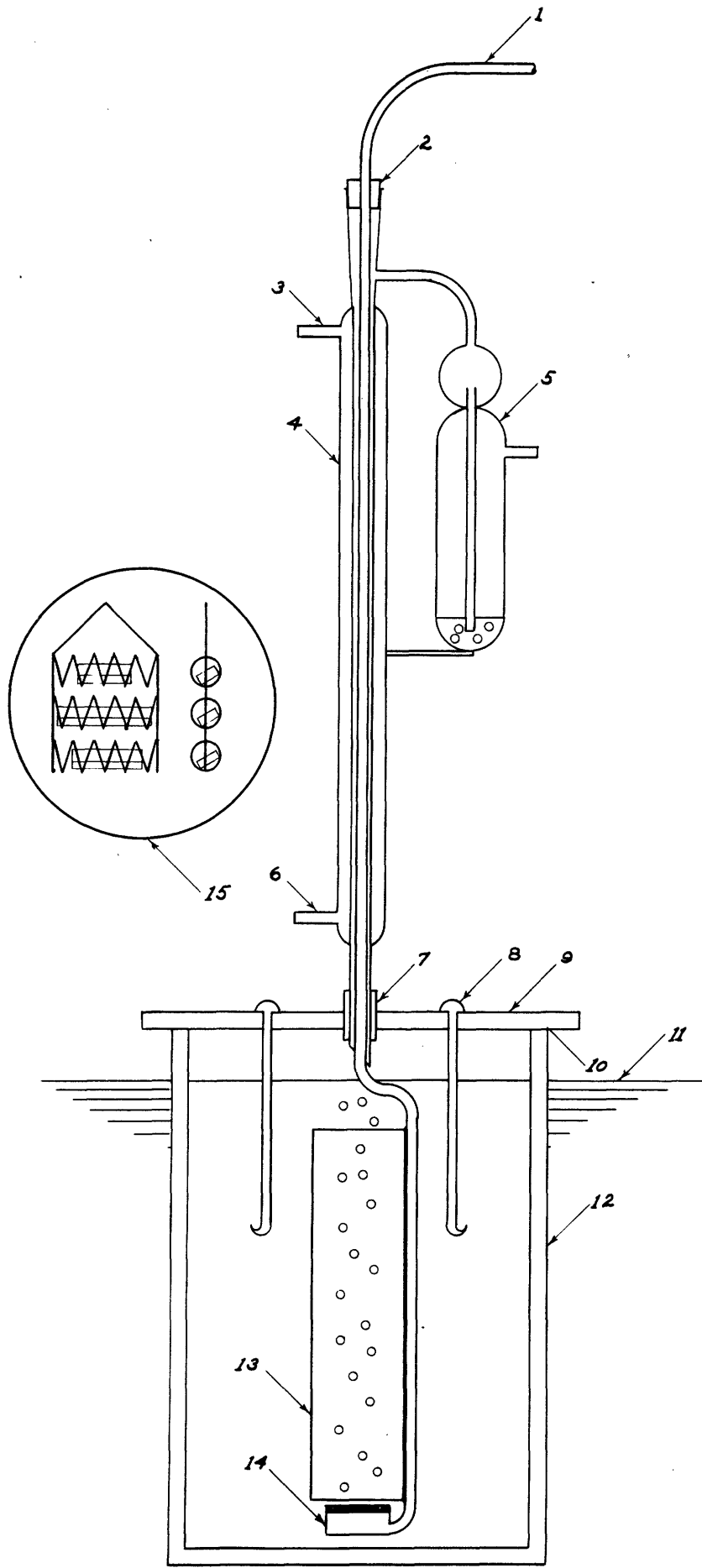


FIGURE 15  
SCHEMATIC DIAGRAM OF CORROSION APPARATUS

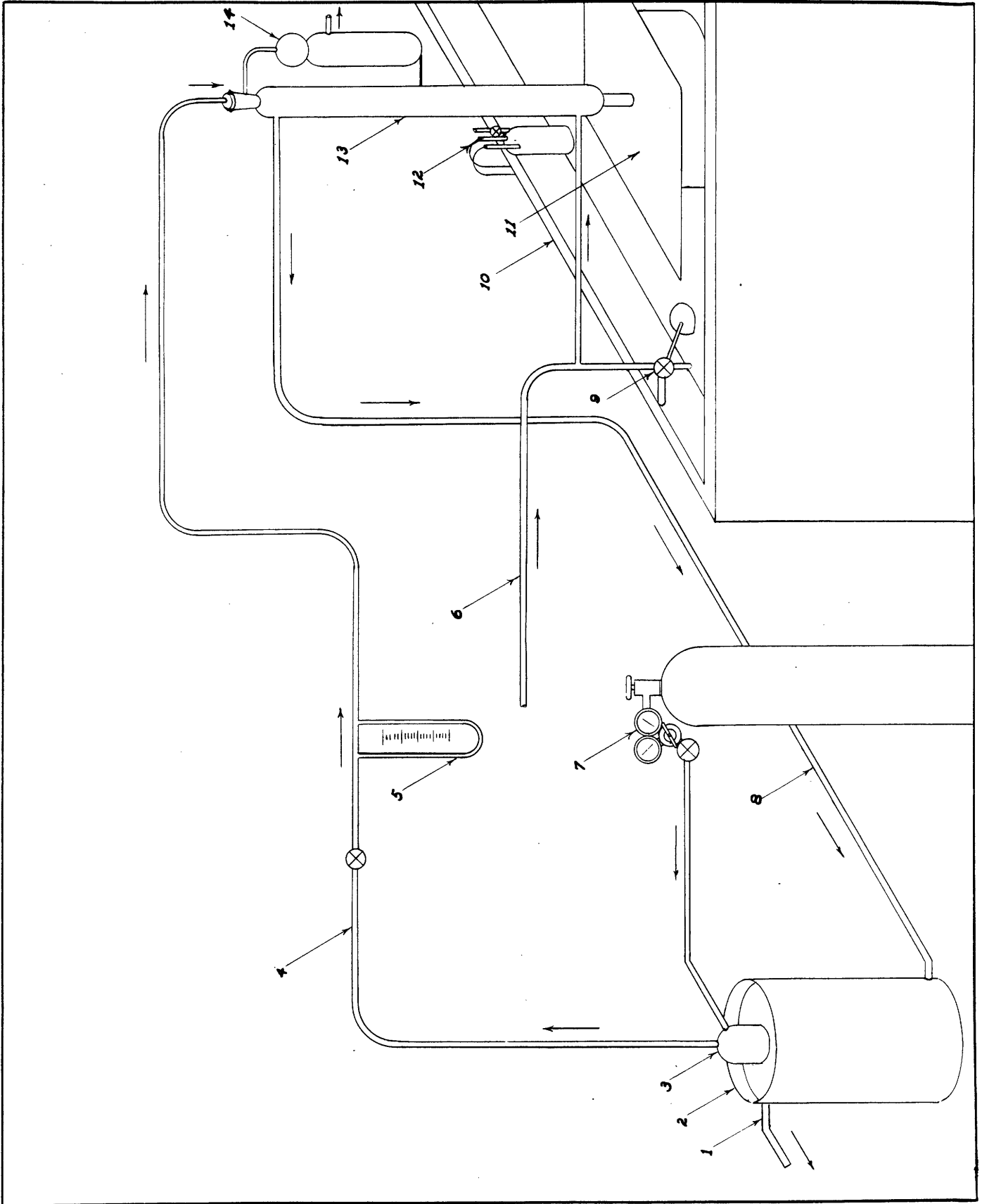
FIGURE 15

Legend

- 1.- Cooling water discharge
- 2.- Cooling tank for oxygen saturator
- 3.- Oxygen saturator filled with acid medium
- 4.- Oxygen feed line
- 5.- Flowmeter with preceding stopcock for controlling gas flow
- 6.- Cooling water inlet
- 7.- Oxygen tank with reduction valve
- 8.- Cooling water return line to saturator tank.
- 9.- Constant levelling device for feed water to constant temperature bath
- 10.- Constant temperature bath
- 11.- Corrosion jar and cover plate
- 12.- Mercury thermostat
- 13.- Water-cooled condenser
- 14.- Air trap

Note: Arrows indicate direction of flow of oxygen and cooling water.





free from grease or films of oil. The surface of the specimens should be free from pits and pores in order that the surfaces may be measured with accuracy, particularly when small specimens must be employed. The grain size of the specimens may cause variations in the results observed, and if the grain size cannot be controlled during the preparation of the specimens, it should at least be known.

All metal samples were prepared in the same manner as described previously. They were pressed from pure metal powders, sintered, fused in the arc furnace, and annealed. Bars were cut from the cast ingots and surface ground on emery belts to give brick-shaped bars. The bars were finish ground on No. 1 emery paper on all six surfaces to insure the plainness of all surfaces. Specimens were selected so that dense bars were obtained with no pores or pits. They were carefully washed to remove all films of oil and grease, rinsed thoroughly in tap water, followed by a rinse in distilled water. This was followed by a wash in benzene, alcohol, and ether, and then storing in a dessicator. The bars were weighed to 0.1 milligram and were carefully measured with a micrometer caliper to 0.0001". The area of each surface was carefully determined in order to obtain the

total surface area of each bar.

Three specimens of each composition were prepared. This permitted the periodic removal of specimens from a corrosion run and provided a means of determining the variation in rate of the corrosion of each specimen. The periodic removal of specimens also served as a check on the results obtained.

The only factor which could not be controlled in obtaining specimens of uniform history was the grain size. Although grain size control was impossible, the average diameter of the grains in the specimens of each composition was known.

After each corrosion run was completed, the specimens were carefully washed, dried, and weighed as described above. Where corrosion was pronounced, the bar was resurfaced, measured and weighed so that it could be used for further study. Where films had formed on the surface, they were wiped off, where possible, or the film was carefully brushed off to prevent accidental removal of uncorroded metal. The metal surface of each specimen was examined under a low power microscope before and after the corrosion run.

The concentration of the corroding medium was checked before and after each run, and in no case was the variation in concentration greater than 0.8%.

Three corrosion jars were placed in the constant temperature bath. Each jar contained specimens of four compositions, with three specimens of each composition in each hanger. The four glass hooks on which each of the four hangers were placed were placed radially around the bubbler chimney. After each period during a run, the cover plates were removed and a sample of each composition removed from the hangers. By this means, the simultaneous testing of a complete series of alloys under identical conditions could be accomplished.

C.- The Corrosion Rate of Tantalum-Molybdenum Alloys  
in Concentrated Sulfuric Acid

The corrosion run in concentrated sulfuric acid was continued for 504 hours in an oxygen-saturated solution at 55°C. Specimens were removed after 210, 406, and 504 hours. Where corrosion had occurred, microscopic examination indicated that the corrosion was uniform in nature. The slight film formed was light brown in color and could be wiped off readily. There was no indication that the molybdenum had been preferentially attacked in the alloys.

The corrosion occurred in the molybdenum-rich alloys, and, generally, was of the order of one milligram per decimeter per day, including the specimens of pure molybdenum. The corrosion rate of the alloys is presented in Table 10. It will be noted, particularly in Figure 16, that the corrosion ceases abruptly at the composition of 50 atomic percent each of tantalum and molybdenum. From this composition to that of pure tantalum, no further corrosion of the alloys is observed.

Tantalum has been reported to be unreactive in concentrated sulfuric acid, and this passive nature continues as molybdenum is added, until 60 atomic

percent molybdenum is added. At this point, the alloy corrodes at a very small rate.

The corrosion rate of the alloys rich in molybdenum was uniform, and did not vary with time. The loosely adherent film formed gave no protection to the metal surface and did not retard the rate of corrosion.

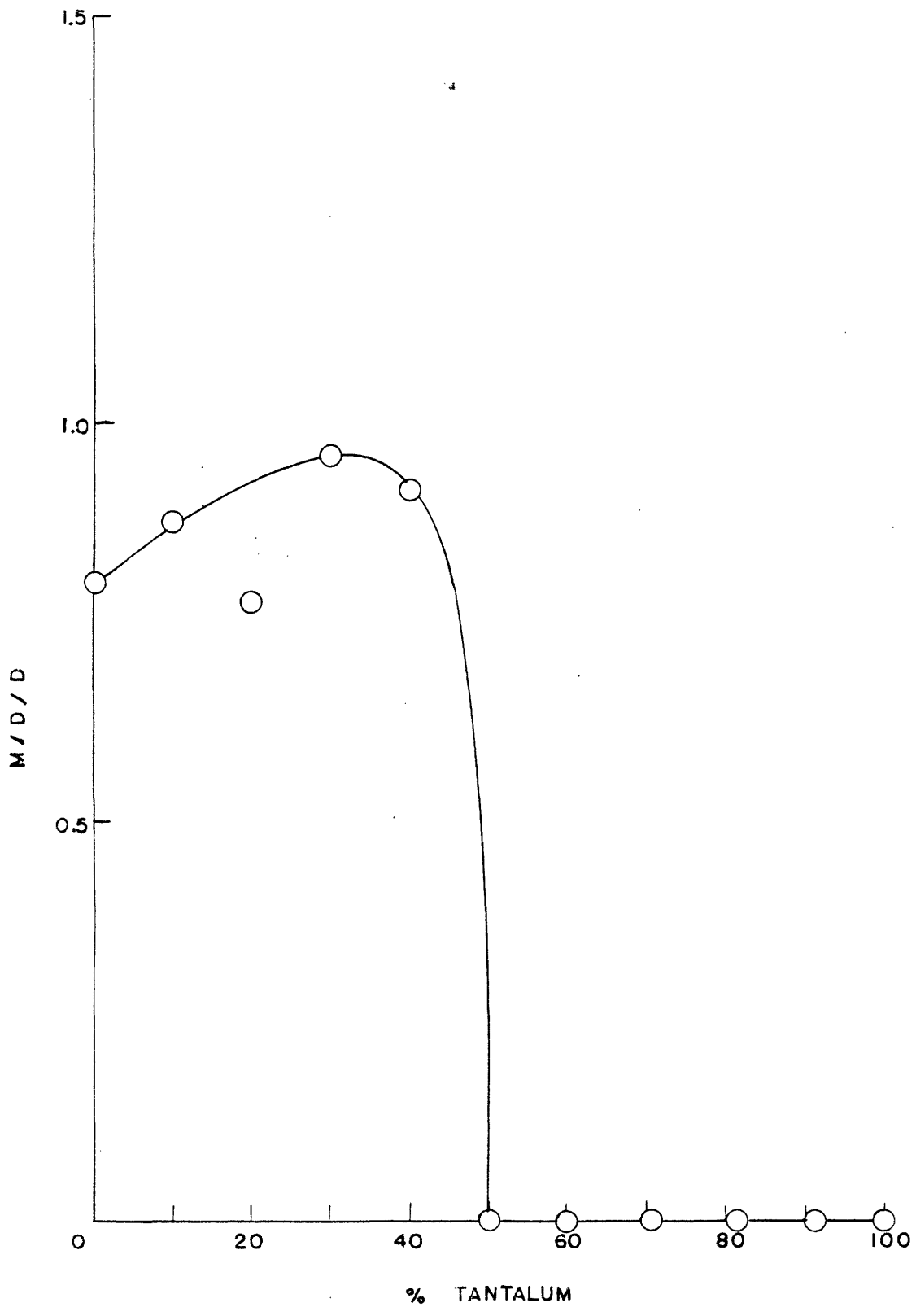
Table 10

Corrosion Rate of Tantalum-Molybdenum Alloys in  
Concentrated Sulfuric Acid at 55°C.

<u>Sample No.</u>	<u>% Mo</u>	<u>% Ta</u>	<u>Average Corrosion Rate Milligrams per decimeter per day</u>
101	100	0	0.80
102	89.90	10.10	0.88
103	79.92	20.08	0.78
104	69.08	30.02	0.96
105	60.04	39.96	0.92
106	50.53	49.97	0
107	38.79	61.21	0
108	28.53	71.47	0
109	17.23	82.77	0
110	8.58	91.42	0
111	0	100	0

FIGURE 16  
THE CORROSION RATE OF TANTALUM-MOLYBDENUM  
ALLOYS IN CONCENTRATED SULFURIC ACID AT  
55°C., AS A FUNCTION OF COMPOSITION





D. - Corrosion Rate of the Alloys in Concentrated Hydrochloric Acid

The rate of corrosion of the alloys in concentrated hydrochloric acid, saturated with oxygen at one atmosphere, at a temperature of 55°C. was determined. Specimens were removed from the corrosion jars after 138, 239, and 256 hours. The molybdenum-rich alloys were corroded at a rate of approximately 2 milligrams per decimeter per day. All specimens which corroded were covered with a thin, brown to straw-colored film which was readily washed off the metal surfaces. The film was transparent, and when removed, microscopic examination of the metal surfaces revealed that the corrosion was uniform in nature. There was no evidence of pitting.

The average corrosion rates of the three specimens of each composition are presented in Table 11. The data for specimen No. 108, containing 30 atomic percent molybdenum and 70 atomic percent tantalum, were rejected. There was evidence that while the specimens were being handled, small segments had chipped out of the edges of the bars, thereby giving abnormal weight losses. The corrosion rate of the alloys in concentrated hydrochloric acid is slightly

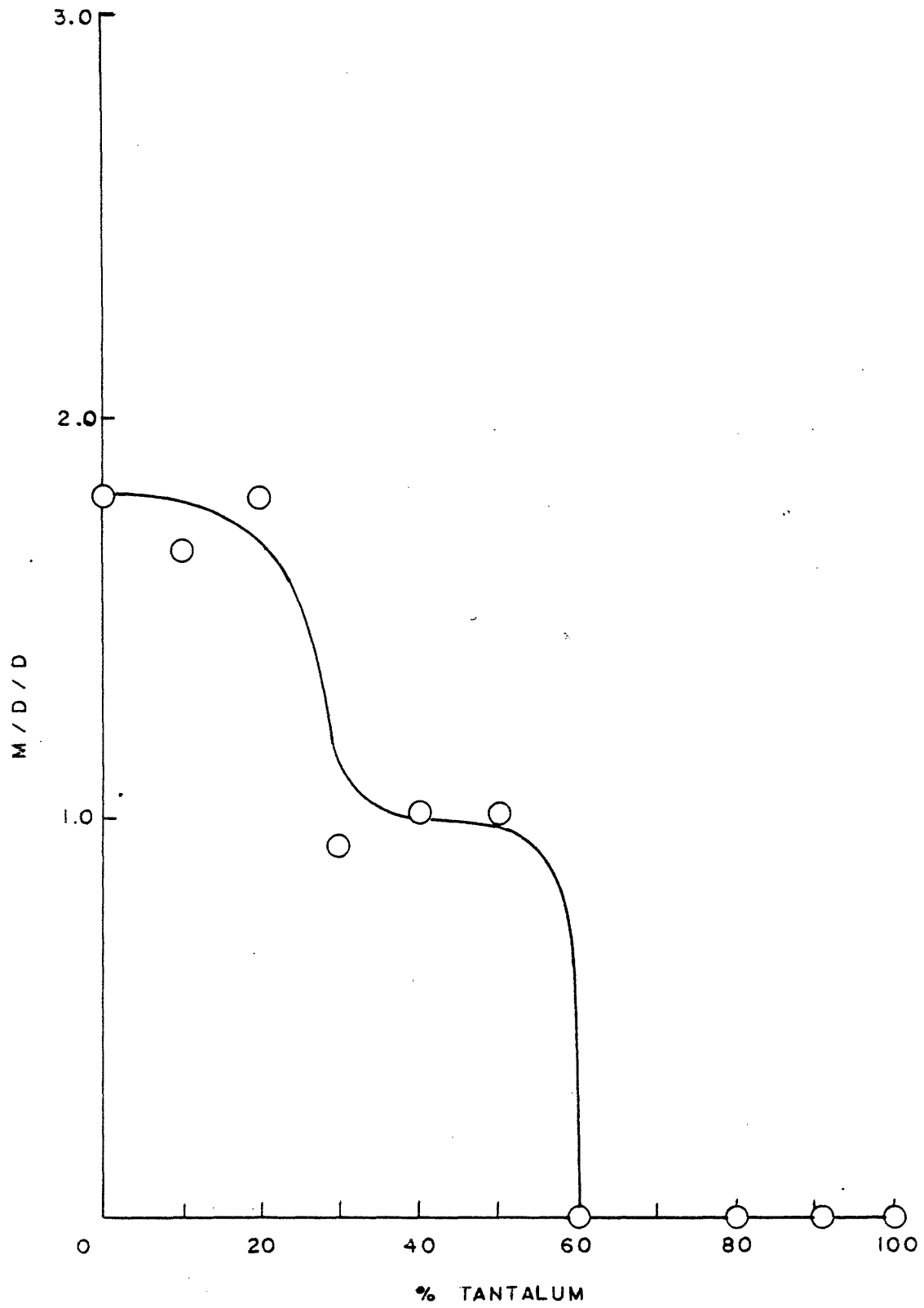
greater than that in concentrated sulfuric acid, and the attack in hydrochloric acid continues over a greater range of composition. The curves of the corrosion rate in the two media are smaller, as may be seen by comparing Figures 16 and 17. As in the case of sulfuric acid, the tantalum-rich alloys are not attacked by hydrochloric acid.

Table 11

Corrosion Rate of Tantalum-Molybdenum Alloys in  
Concentrated Hydrochloric Acid at 55°C.

<u>Sample No.</u>	<u>% Mo</u>	<u>% Ta</u>	<u>Average Corrosion Rate Milligrams per decimeter per day</u>
101	100	0	1.80
102	89.90	10.10	1.67
103	79.92	20.08	1.80
104	69.08	30.02	0.93
105	60.04	39.96	1.08
106	50.53	49.97	1.03
107	38.79	61.21	0
108	28.53	71.47	
109	17.23	82.77	0
110	8.58	91.42	0
111	0	100	0

FIGURE 17  
THE CORROSION RATE OF TANTALUM-MOLYBDENUM  
ALLOYS IN CONCENTRATED HYDROCHLORIC ACID  
AT 55°C., AS A FUNCTION OF COMPOSITION



E. - The Corrosion of Tantalum-Molybdenum Alloys  
in Concentrated Nitric Acid

The corrosion rate of the alloys in oxygen-saturated, concentrated nitric acid, maintained at a temperature of 55°C., was determined after a period of 330 hours. Specimens were removed after 139, 240, and 330 hours, in order to determine the variation in rate of corrosion with time. Microscopic examination of the alloys revealed that where corrosion had occurred, the films formed were dense and hard, and could not be wiped off. Corrosion occurred only in the molybdenum-rich alloys, from pure molybdenum to the alloy containing 70 atomic per cent molybdenum and 30 atomic per cent tantalum. From the alloy containing 60 atomic per cent tantalum to pure tantalum, no further corrosion of the specimens was observed. The corrosion rate of the alloys is presented in Table 12.

The film formed on the specimens of pure molybdenum was white to bluish white in color. When removed, the film came off in flakes and appeared to be dense and quite hard. The shape of the flakes was identical to that of the grains which appeared when the film was removed. The metal was uniformly attacked over the entire surface of the specimen, and, although

the grain boundaries were clearly visible to the naked eye, microscopic examination did not reveal a preferential attack of the grain boundaries.

It was also observed that the corrosion rate varied considerably with time. The film formed apparently acts as a barrier to the continued oxidation of the metal surface by the nitric acid, and at the end of 330 hours, the rate of corrosion had levelled off. This is graphically portrayed in Figure 18 A.

On the alloy composed of 90 atomic percent molybdenum and 10 atomic percent tantalum, the film formed was bluish-white in color and was quite hard. It was difficult to remove, and did not flake off as in the previous case. Beneath the film, microscopic examination of the metal surface indicated that the corrosion was uniform and not of the dezincification or preferential type. However, there was indication of preferential attack of particular grains, and that the attack was greatest perpendicular to the longitudinal axis of the grains, and least parallel to the longitudinal axis. Again, it was found that the corrosion rate decreased with time, but did not decrease as rapidly as in the case of pure molybdenum.



The transparent, straw-colored film formed on the surface of the specimens composed of 80 atomic percent molybdenum and 20 atomic percent tantalum was very hard and firm. It was difficult to remove, even with brushing. The surface of the metal beneath the film had been attacked uniformly, and there was no evidence of preferential attack of any kind. As shown in Figure 18 A, the corrosion rate of the alloy decreased slowly with time.

As in the previous case, a very hard, thin, transparent, straw-colored film formed on the alloy composed of 70 atomic percent molybdenum and 30 atomic percent tantalum. The corrosion rate of this alloy was of the order of 0.6 milligrams per decimeter per day.

No corrosion was observed in the alloys composed of 40 to 100 atomic percent tantalum. Figure 18 B,C, shows the rapid decrease in the corrosion rate of the alloys from pure molybdenum to 70 atomic percent molybdenum, and the complete cessation of attack by nitric acid beyond this composition.

Table 12

## Corrosion Rate of Tantalum-Molybdenum Alloys in Concentrated Nitric Acid at 55°C.

Sample No.	% Mo	% Ta	Time Immersed (hours)	Corrosion Rate as Milligrams per decimeter per day	
				Individual Specimens	Weighed Average
101	100	0	139	292.06	172.06
			231	160.55	
			331	129.70	
102	89.90	10.10	139	94.51	79.91
			231	86.91	
			331	68.88	
103	79.92	20.08	139	10.46	6.16
			231	6.26	
			331	4.27	
104	69.08	30.02	139	0	0.19
			231	0	
			331	0.579	
105	60.04	39.96	139	0	0
			231	0	
			331	0	
106	50.53	49.47	139	0	0
			231	0	
			331	0	
107	38.79	61.21	139	0	0
			231	0	
			331	0	
108	28.53	71.47	139	0	0
			231	0	
			331	0	

Table 12 (cont.)  
 Corrosion Rate of Tantalum-Molybdenum Alloys in Concentrated Nitric Acid at 55°C.

Sample No.	% Mo	% Ta	Time Immersed (hours)	Corrosion Rate as Milligrams per decimeter per day	
				Individual Specimens	Weighted Average
109	17.23	82.77	139	0	0
			231	0	0
			331	0	0
110	8.58	91.42	139	0	0
			231	0	0
			331	0	0
111	0	100	139	0	0
			231	0	0
			331	0	0

FIGURE 18  
THE CORROSION RATE OF TANTALUM-MOLYBDENUM  
ALLOYS IN CONCENTRATED NITRIC ACID AT 55°C.

FIGURE 18-A  
THE CORROSION RATE OF THREE TANTALUM-MOLYB-  
DENUM ALLOYS IN CONCENTRATED NITRIC ACID AT  
55°C., AS A FUNCTION OF TIME

- 1.- Pure Molybdenum
- 2.- 10 Atomic Percent Molybdenum  
90 Atomic Percent Tantalum
- 3.- 20 Atomic Percent Molybdenum  
80 Atomic Percent Tantalum

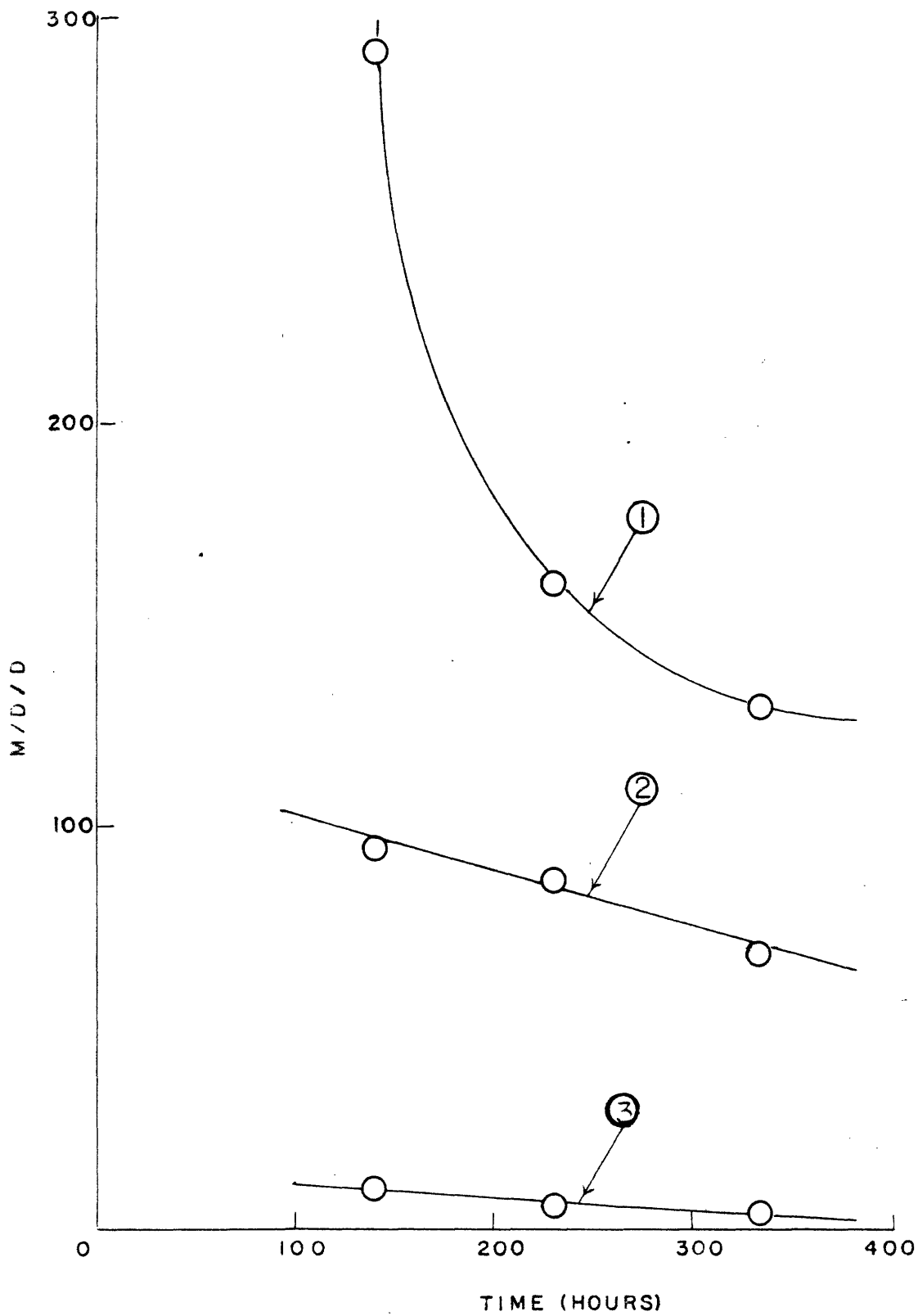


FIGURE 18 B

THE CORROSION RATE OF TANTALUM-MOLYBDENUM  
ALLOYS IN CONCENTRATED NITRIC ACID  
AT 55°C., REMOVED PERIODICALLY AS A  
FUNCTION OF COMPOSITION

- 1.- Removed after 139 Hours
- 2.- Removed after 231 Hours
- 3.- Removed after 331 Hours

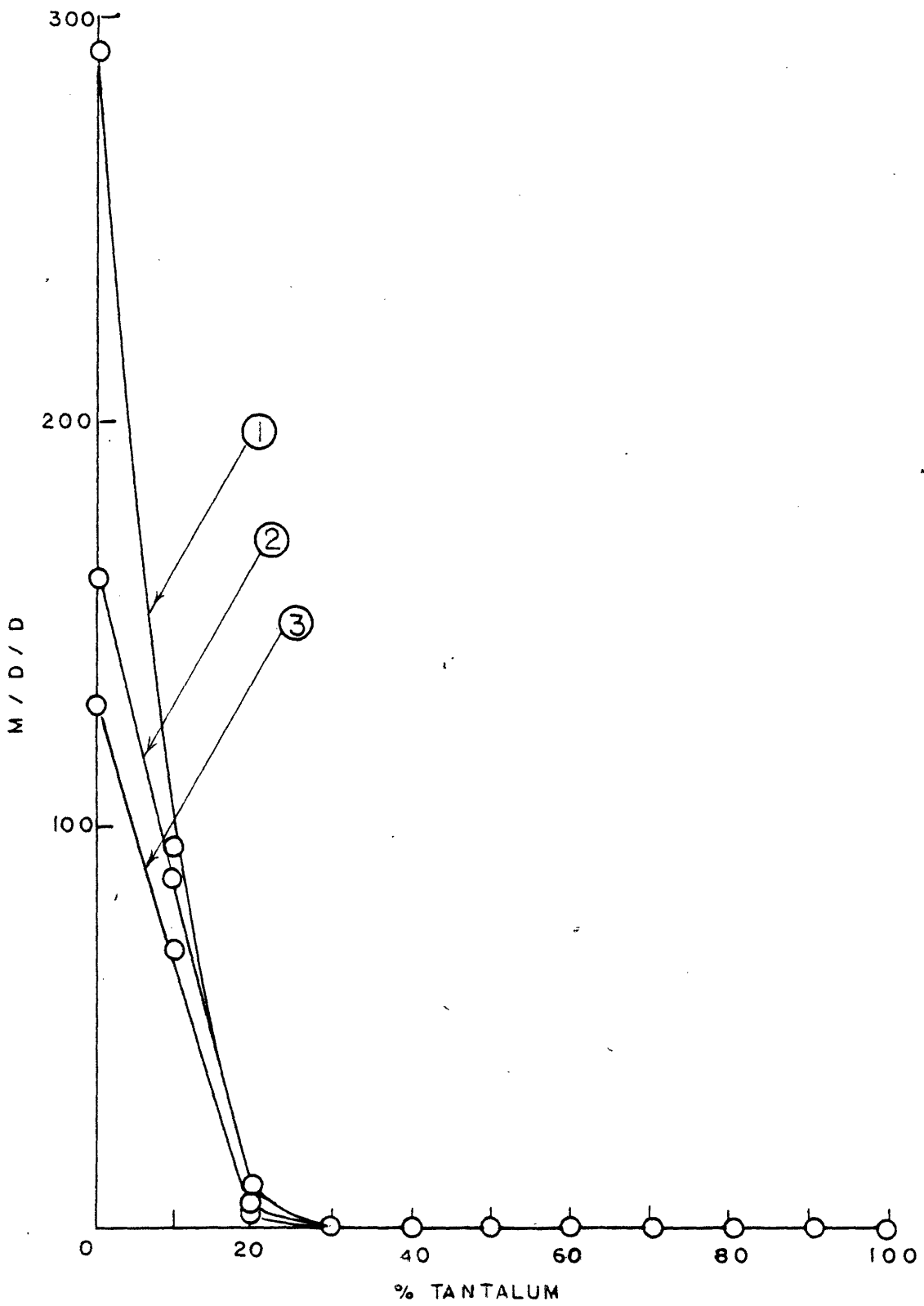
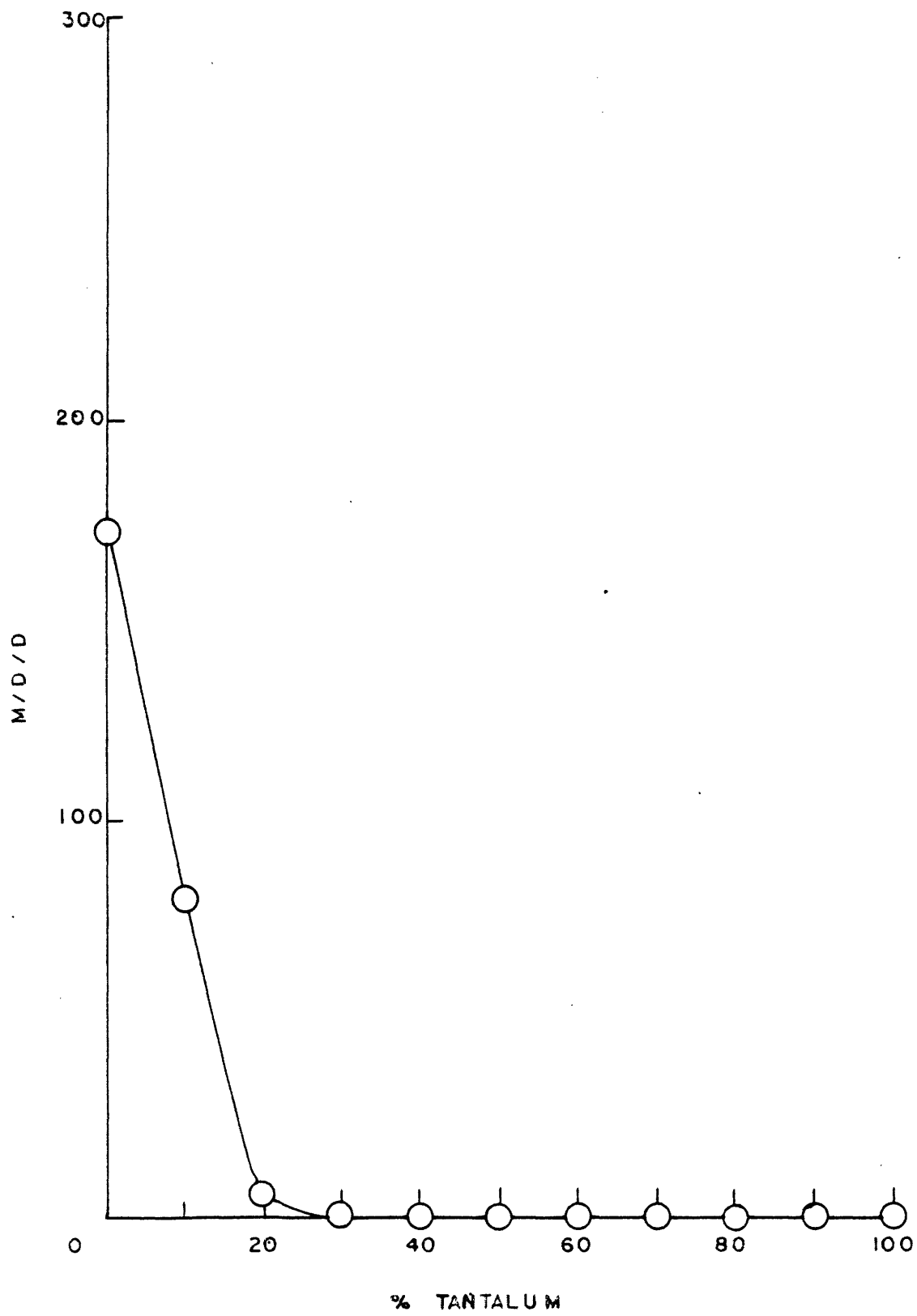




FIGURE 18 C  
THE MEAN CORROSION RATE OF TANTALUM-MOLYBDENUM  
ALLOYS IN CONCENTRATED NITRIC ACID AT 55°C.,  
AS A FUNCTION OF COMPOSITION



#### IV.- Summary

This research has developed a method for the preparation of high melting alloys of tantalum and molybdenum, which is applicable to the preparation of alloys of other high melting metals. Procedures for the metallographic and chemical analysis of the alloys were involved.

Many of the physical properties were investigated, such as the densities, hardness, thermoelectric power, electrical resistivity, and the linear coefficient of thermal expansion.

The corrosion rate of the alloys in concentrated acids was determined. The tantalum-rich alloys were unattacked in sulfuric, hydrochloric, and nitric acids, whereas the molybdenum-rich alloys were attacked at an increasing rate from sulfuric acid to hydrochloric acid to nitric acid.

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PART II

PART II  
AMPLIFICATION

I.- Preparation of the Alloys

A.- Introduction

Considerable time and effort were expended upon the investigation of methods of preparation of the alloys. Attempts to use existing equipment were in all cases unsuccessful. The preparation of tantalum and molybdenum alloys required special apparatus, which was developed during this research.

B.- Initial Scope of the Research

It was planned to investigate a large number of binary alloy systems of tantalum with such elements as vanadium, columbium, tungsten, molybdenum, chromium, iron, cobalt, nickel, etc. The powdered metals were milled, pressed, and fused in an arc furnace borrowed for this purpose from the Metallurgical Project at M. I. T. The melts obtained were very poor in quality, and the apparatus was not designed to utilize a pure inert atmosphere. Tank argon was used without purification, and it was found that there was a considerable amount of non-metallic inclusions in the melts. The use of un-sintered pressed compacts was unsatisfactory, as they yielded porous melts, and, in practically every instance, the compacts exploded when the arc was struck on the compact. Metallographic examination of the

products obtained from these melts showed pores, impurities, and a complex array of unknown phases in the matrix when alloys of tantalum and iron, cobalt, nickel, and silicon were prepared. As the phase diagrams of these alloys are not known, completely, it would have been necessary to develop the phase diagram before continuing with a study of the properties of the alloys. It was therefore essential that a system be chosen where the phase diagram was known, and that only a single system be investigated in order that a more complete study could be accomplished. As von Bolton had demonstrated that tantalum and molybdenum form a continuous series of solid solutions, this system was selected.

#### C.- Arc Furnace

As mentioned above, the initial furnace used did not produce satisfactory results. The presence of impurities, and the inability to obtain ingots of fairly regular shape were the reasons for abandoning this method.

#### D.- Sintering by Induction Heating

A furnace similar to that shown in Figure 1 was constructed, together with a large capacity vacuum system. Pressed compacts of the alloy compositions



desired were made up and sintered in the furnace at temperatures ranging from approximately 1800 to 2000°C. The sintered compacts obtained were quite porous. The porosity of the pure molybdenum compacts was roughly 10%; the porosity was not uniform and varied from one area to another throughout the mass of the compact. As the percentage of tantalum increased, the porosity increased, and as dense alloys could not be obtained by this method, it, too, was discarded.

The Metallurgical Section of Watertown Arsenal made available for use in this research a vacuum induction furnace of very large capacity. The furnace was fitted with a graphite heater for the specimens, instead of requiring the specimens to serve as their own heaters. It was realized that there was danger of increasing the carbon content of the tantalum in the presence of a hot mass of carbon; nevertheless, alloys were sintered in the furnace. During preliminary runs, sample alloys were sintered at a temperature of approximately 1500°C. for one hour. The resulting alloys were analyzed for the carbon content, and it was found that the carbon content of the tantalum, which was originally 0.03%, had increased over 30 times during the period in which the specimens were in the furnace.

As there was no way to redesign this furnace to eliminate the carbon heater without very extensive modifications, other methods of preparing the alloys had to be investigated.

#### E.- Resistance Sintered Alloys

The Fansteel Metallurgical Corporation kindly offered to prepare a series of alloys by resistance sintering. Tantalum and molybdenum powders were mixed in the desired proportions and tumbled. They were next pressed in a die to give cold-pressed bars roughly 6"x1/8"x1/4". Each bar was placed in series with water-cooled terminals in a vacuum system. A large amperage current was passed through the bar heating it to the desired sintering temperature. The maximum temperature was held for one hour, and the bar was then allowed to cool to room temperature in vacuo.

However, metallographic examination of the specimens showed them to be widely varying in their degrees of porosity. As several of the intermediate compositions proved to be very brittle, it was not possible for the Fansteel Metallurgical Corporation to forge them with the equipment they had available. As discussed in Part I, attempts to forge the specimens in a sealed iron envelope proved unsuccessful, and these alloys could

not be used for further work. However, in testing the corrosion apparatus described in Part I, a set of these alloys was used. Further evidence that they were unsatisfactory even for this work was found. The porous bars filled with the corroding medium, and it was impossible to remove the internal corrosion products and the unreacted acid trapped inside the bar. Consequently, erratic results were obtained.

#### F. Modified Arc Furnace

As all previous methods of preparing the alloys had proved unsatisfactory, attempts were made to improve on the design of the original furnace used. First, the improved design called for a system for removing all traces of impurities from the argon, such as water vapor, nitrogen and oxygen. An improved furnace cover was constructed which provided greater flexibility for the moveable electrode and an efficient gas seal. A larger water-cooled crucible was made to permit the melting of larger compacts and to facilitate cleaning after each melt. The entire system was built as a mobile, compact unit, with vacuum tight lines leading to and from the furnace proper.

A portable heavy-duty Wilson welding generator, operating on 250 volts A. C., and delivering up to 35

to 40 volts at 450 amperes D. C., served as the source of power for the furnace. Initial practice melts were successful, and it was demonstrated that dense, fairly symmetrical ingots could be produced. Further tests were made on compacts that had been pressed but not sintered, and on the sintered compacts discussed in Section D. It was evident that sintering green compacts before fusion in the arc furnace produced dense ingots with few if any pores, and greatly simplified the melting of the compacts. Green or un-sintered compacts cracked or exploded during melting and greatly increased the difficulties of obtaining symmetrical ingots.

G.- Preparation of Specimens for Corrosion Studies and Determination of Physical Properties

Sectioning the cast and annealed ingots proved to be one of the most time-consuming and troublesome problems. After attempts had been made to section the alloys with several different cut-off wheels available at the Institute, it was found that only one machine could cut the specimens and produce parallel sections from the ingots. The alloys were observed to be very abrasion resistant, and great difficulty was encountered in finding wheels that could cut the material without

breaking. The thin rubber-bonded discs discussed in Part I were very satisfactory and few were broken. The specimens were mounted in the cut-off machine between lead sheets. The lead sheets served to hold the specimens steadier and reduced breakage of the more brittle alloys. Although it required only ten to fifteen minutes to make a cut 1" deep in a specimen  $\frac{1}{4}$ " thick, in ingots of pure molybdenum, from one to one and one-half hours were consumed in making a single cut through similar ingots of the other compositions.

The pieces of metal cut from the ingots were then carefully ground to produce the bars required for further study. Special clamps were made to hold the bars in place during the grinding operation, in order to reduce dimensional variations.

II.- Biographical Note

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