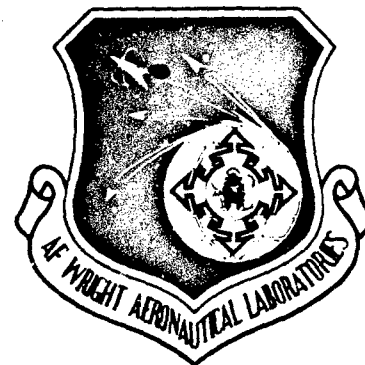


AFWAL-TR-84-4141

A STUDY OF RHENIUM
AS AN ALTERNATE SUBSTRATE MATERIAL
FOR
IMPREGNATED DISPENSER CATHODES



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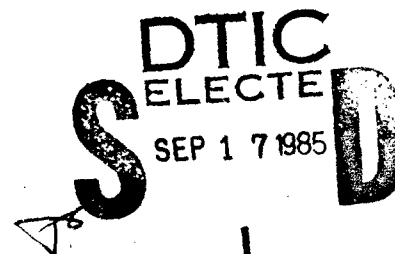
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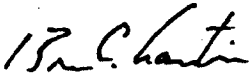
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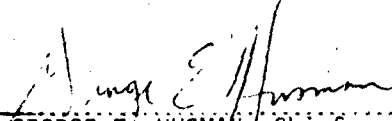
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20. ABSTRACT (continued)

Cathodes impregnated with 5:3:2 or 4:1:1 barium-calcium-aluminate were tested for emission performance and compared to tungsten cathodes. A guard ring structure was installed around the cathode to suppress edge effects.

Results indicated that rhenium can be fabricated into a working cathode. Fabrication techniques are not completed, and optimization methods need to be studied. Results from emission testing showed 4:1:1 to be the impregnant of choice for a rhenium matrix due to little or no emission from a 5:3:2 impregnated cathode. Testing also proved that activation procedures must be altered according to the metal used. Recommendations for methods of emission enhancement and future studies were made.

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1.0 INTRODUCTION

Increased performance demands for space-borne traveling wave tubes (TWT's) are immediately reflected in enhanced expectations for cathodes applied in such tubes. Load requirements exceeding 1 A/cm^2 over lifetimes greater than 40,000 hours coupled with lower operating temperature requirements have pushed the state-of-the-art tungsten matrix cathode to its performance limits.

In order to assure long-term stability of the cathode matrix material, it may be desirable to use a single phase, pure metal substrate. It is well known in the cathode field that the high work function metals of the platinum group, specifically iridium, osmium, and rhenium, enhance emission performance in comparison to tungsten. Since the processing of sintered compacts of pure iridium and pure osmium is known to be impractical or impossible, rhenium remains the likely candidate for study.

This program was undertaken with the objective of developing techniques required to fabricate rhenium dispenser cathodes, test the emission performance of such cathodes, and compare their performance with that of tungsten cathodes. The work could be used as a basis to determine the feasibility of rhenium as an alternate cathode matrix material.

2.0 TASK DEFINITION

As defined in the statement of work for this contract, the program was to be carried out in five phases.

The first phase was to research sources and procure rhenium powder suitable for our purposes. The program required powder with an average particle size of four to eight micrometers. Once procured, the powder had to be chemically and physically characterized. Phase two consisted of procurement and characterization of the impregnants and their raw material constituents. When this was finished, phase three, which involved the study of fabrication parameters of a porous rhenium pellet, was begun. Pressing pressures, sintering temperatures, and sintering times were the factors of concern. Due to their small dimensions the pellets were to be die-pressed. Upon successful completion of phase three, fabrication of impregnated cathodes initiated the fourth task. This

involved attempts at various machining techniques and methods of mounting a pellet into a support structure. The fifth and final phase embodied the emission testing and evaluation stage of the program. Comparison to tungsten cathodes and recommendation for future work were to be proffered.

3.0 HISTORICAL REVIEW

As the technology of microwave tubes has evolved, the demands on the cathodes applied in such tubes have increased. Emphasis moved from the oxide cathode to the tungsten dispenser cathode. Space-borne traveling wave tubes (TWT's) require longer lifetimes, increased loadings and lower operating temperatures. SATCOM systems extending to the 20/30 GHz band, loads exceeding 1 A/cm², and operating temperatures near 1850° C Brightness are realistic, but not mutually consistent objectives. The tungsten dispenser cathode is becoming a compromise in meeting these objectives so alternative materials are being sought.

Various methods of emission enhancement have been attempted, but all have had their faults. A few of the problems have been expense, short lifetimes, and instability. The osmium-coated tungsten cathode and the tungsten-iridium mixed metal matrix cathode are two notable examples of enhanced emission capability. Unfortunately, both types involve a reaction between two metals which brings about the question of their stability throughout lifetime.

In order to assure long-term stability of the matrix material, it may be desirable to use a single phase, pure metal substrate. It is well known in the field that the high work function metals of the platinum group, specifically iridium, osmium, and rhenium, enhance emission performance in comparison to tungsten.

Powder metallurgical processing difficulties have prevented the use of osmium and iridium as substrate materials. It is likely that chemical reactions in the rhenium substrate necessary to produce adequate supplies of surface activating materials--barium metal and/or barium-oxygen--will be similar to those observed in tungsten.

An extensive literature search provided very little information on previous work. Hata and Kai¹ found a 65% dense rhenium cathode to be inferior in emission in comparison to a tungsten cathode. Their studies included only 5:3:2 impregnant. Pulsive zero field emissions at 1125°C were 5 A/cm² and 0.8 A/cm² for tungsten and rhenium respectively. One year later Hata and Koitobashi² reported emission performance of a co-compressed rhenium cathode to be superior at all temperatures compared to a 5:3:2 impregnated tungsten cathode. The rhenium cathode was a co-compressing of rhenium with a triple carbonate in a 2:1 ratio by weight. The tungsten cathode was sintered to a 78% density and impregnated.

Although these studies involved two types of rhenium cathode, they mutually agree that powdered rhenium metal can be fabricated into an emitting cathode. The capabilities of such a cathode are still questionable, but the knowledge gained on dispenser cathode operation has increased greatly. Consequently, the likelihood of much better emission performance has improved.

4.0 EXPERIMENTAL APPROACH

The first step of the program was to procure rhenium powder that met the requirements of the contract. They included an average particle size of 6 to 7 microns and a particle size distribution that was as narrow as practical. Once procured, the powder was analyzed for chemical impurities with spark source photoemission techniques. The samples were also tested for carbon and sulfur content. Scanning electron microscopy was used to characterize the shapes of the discrete particles and to develop a feel for their degree of agglomeration.

The impregnants used for the study were manufactured in-house. They were calcined mixtures of BaCO₃:CaCO₃:Al₂O₃ in the molar ratios of 4:1:1 and 5:3:2.

The raw materials were mixed using a ball-milling, dry mixing procedure. The batch size was approximately 300 grams, and duration of mixing was approximately 30 minutes.

Upon completion of mixing, the materials were calcined for 18 hours at 1150°C to 1200°C in an air furnace. Immediately upon cooling, the material was removed, weighed to verify complete weight loss from the carbonate

decomposition, and appropriately stored for protection from atmospheric moisture.

All cathodes fabricated during the project used the same impregnant lots. Samples from each of the 411 and 532 were subjected to x-ray diffraction (XRD) analysis. The patterns for these materials are provided for reference in Figures 1 and 2 (pages 7 and 8), providing values of two theta, d-spacing, measured intensity in counts per second, and relative intensity (see corresponding data tables, Tables 1 and 2, on pages 9 and 10). The diffraction patterns were obtained using Cu K-alpha radiation.

The most important area of focus was ascertaining the fabrication parameters of a porous rhenium matrix. Semicon's experience with tungsten processing served as a basis from which to work. The contract called for pellets of 80% of theoretical density, so processing parameters were varied with that goal in mind. It had also been stipulated that the cathodes would be .100 inches in diameter; this allowed die-pressing to be used rather than isostatic pressing without fear of noticeable matrix nonuniformities, and for the sake of expediency. Hence, the parameters of concern were pressing pressure, sintering pressure, and sintering time.

Pressing was done in a simple cylindrical die using a Carver hydraulic laboratory press. When a cohesive pellet was successfully pressed, green densities were determined by measuring diameter and length to + or - .0002 inches, calculating volume, and dividing that into the weight of the pellet.

Raw powder, piled loosely on a tray, was sintered to agglomerate the particles to a point where they had only necked together. The reasons for this were two-fold: a minimum temperature for sintering studies could be established and, it was hoped, more regular shapes could be produced. All firings were done in an atmosphere of dissociated ammonia in a furnace which was capable of temperatures in excess of 2200°C. Temperatures were measured by a disappearing filament optical pyrometer.

Upon completion of this stage, a program of sintering studies was initiated. Pressing pressures, and therefore green densities, were varied along with sintering temperatures and duration of the cycles.

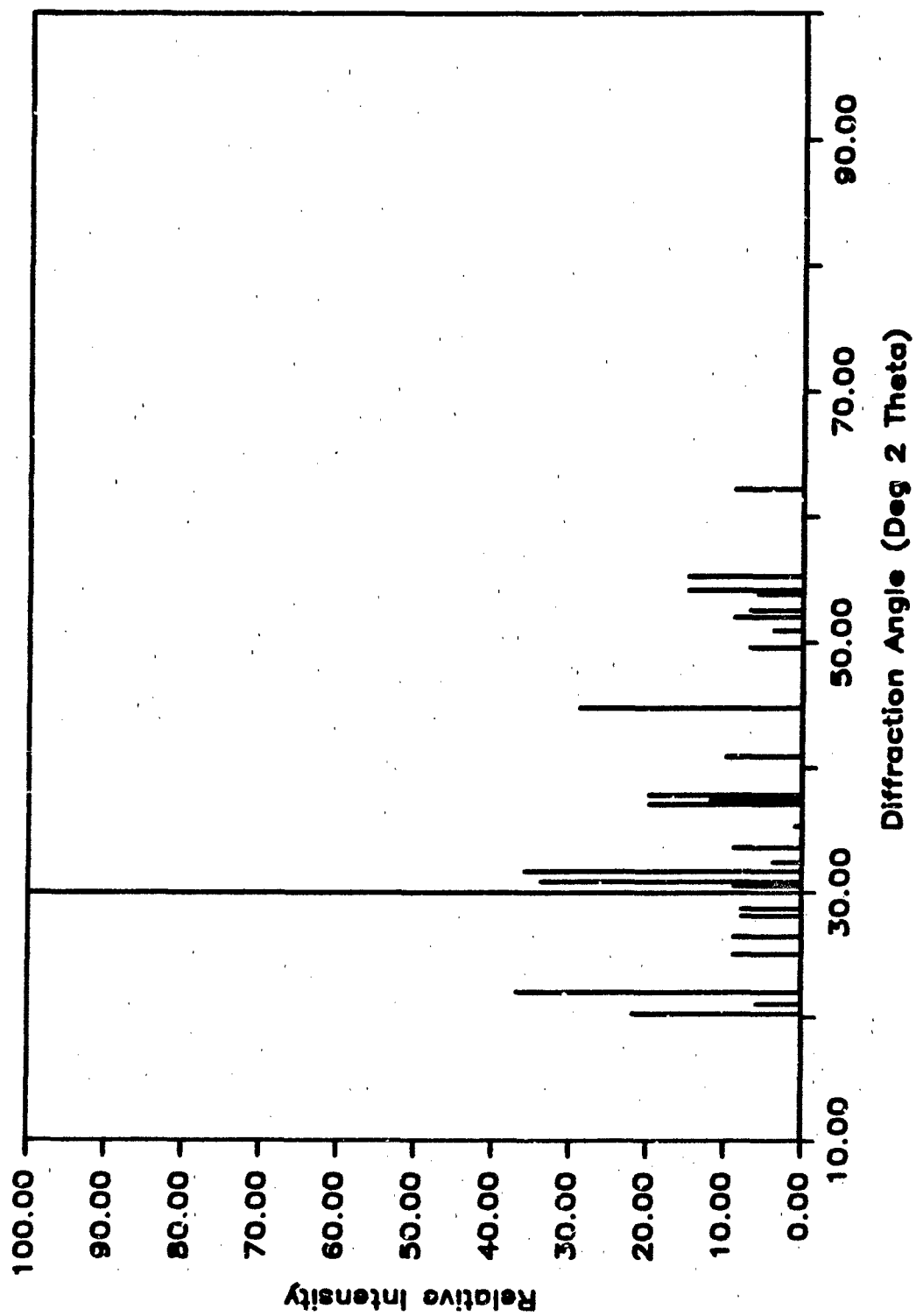


Fig. 1. XRD Pattern for 411 Impregnant

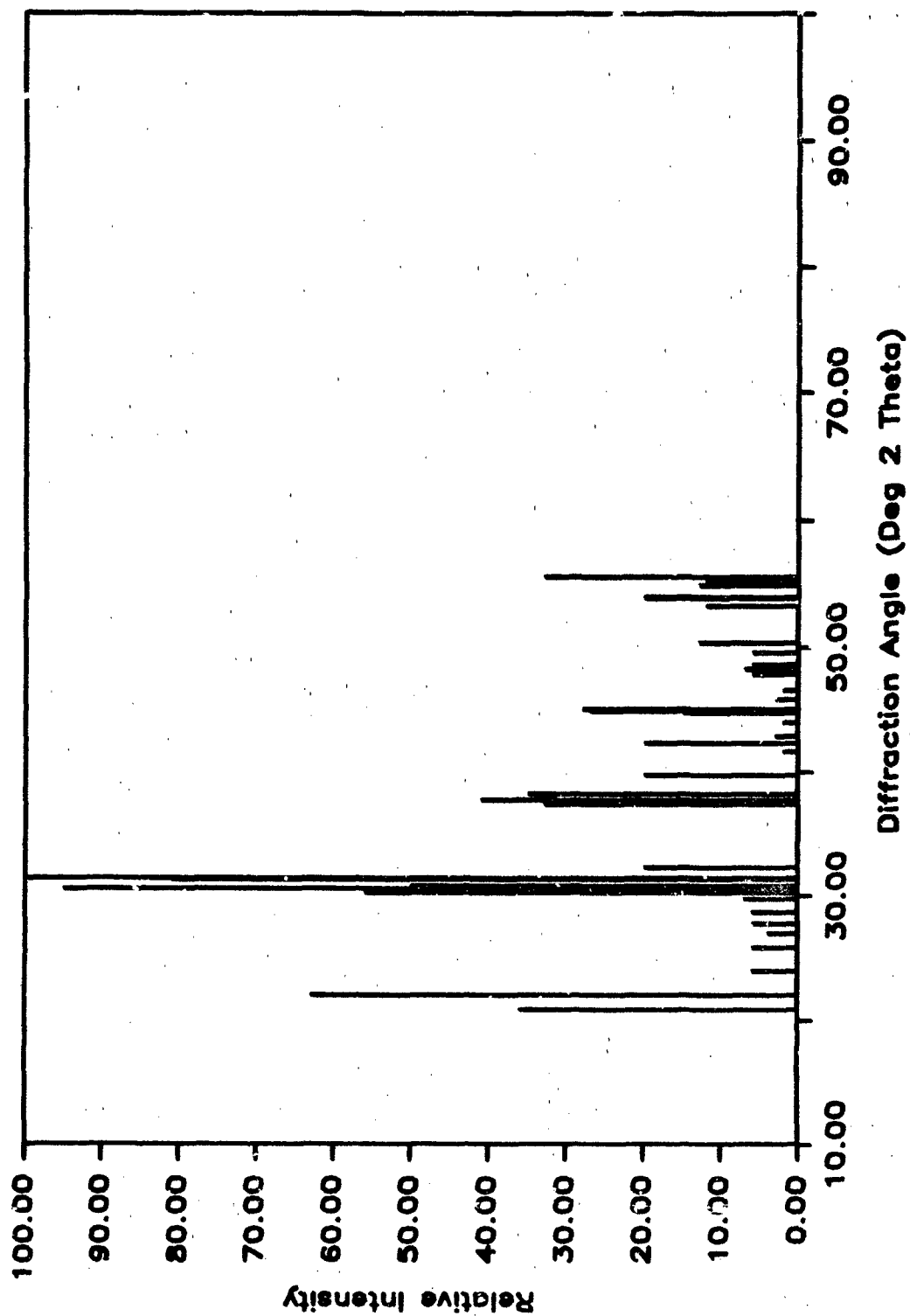


Fig. 2. XRD Pattern for 532 Impregnant

TABLE 1. X-RAY DIFFRACTION DATA FOR 411 IMPREGNANT

Peak No.	2 Theta (Deg)	D-Spacing (Ang.)	Intensity (CPS)	Relative Intensity
1	20.21	4.3901	97.	22.
2	21.00	4.2267	27.	6.
3	21.95	4.0459	165.	37.
4	25.02	3.5560	38.	9.
5	26.45	3.3669	41.	9.
6	28.10	3.1728	33.	8.
7	28.69	3.1089	33.	8.
8	29.98	2.9780	440.	100.
9	30.50	2.9284	40.	9.
10	30.83	2.8978	148.	34.
11	31.67	2.8228	158.	36.
12	32.22	2.7759	2.	6.
13	32.38	2.7625	17.	4.
14	33.53	2.6704	42.	9.
15	33.87	2.6443	6.	1.
16	35.31	2.5397	4.	1.
17	37.06	2.4237	89.	20.
18	37.37	2.4043	53.	12.
19	37.80	2.3779	89.	20.
20	40.89	2.2051	42.	10.
21	44.76	2.0230	128.	29.
22	49.55	1.8381	32.	7.
23	50.94	1.7911	17.	4.
24	52.03	1.7561	39.	9.
25	52.59	1.7388	30.	7.
26	53.86	1.7007	28.	6.
27	54.22	1.6903	64.	15.
28	55.32	1.6592	68.	15.
29	62.18	1.4916	38.	9.

TABLE 2. X-RAY DIFFRACTION DATA FOR 532 IMPREGNANT

Peak No.	2 Theta (Deg)	D-Spacing (Ang.)	Intensity (CPS)	Relative Intensity
1	20.79	4.2689	270.	36.
2	21.99	4.0386	471.	63.
3	23.90	3.7200	42.	6.
4	25.77	3.4541	43.	6.
5	26.93	3.3079	33.	4.
6	27.71	3.2166	44.	6.
7	28.62	3.1163	44.	6.
8	29.71	3.0044	55.	7.
9	30.17	2.9597	415.	56.
10	30.52	2.9265	705.	95.
11	30.75	2.9051	35.	50.
12	31.24	2.8607	606.	81.
13	31.35	2.8509	746.	100.
14	32.21	2.7767	146.	20.
15	37.36	2.4049	244.	33.
16	37.69	2.3846	309.	41.
17	38.18	2.3551	264.	35.
18	39.69	2.2689	150.	20.
19	41.59	2.1696	16.	2.
20	42.31	2.1343	151.	20.
21	42.84	2.1091	21.	3.
22	43.96	2.0579	12.	2.
23	44.71	2.0252	112.	15.
24	44.86	2.0187	202.	27.
25	45.01	2.0123	213.	28.
26	45.80	1.9795	23.	3.
27	46.52	1.9505	13.	2.
28	47.80	1.9012	44.	6.
29	48.29	1.8864	54.	7.
30	48.57	1.8728	44.	6.
31	49.54	1.8384	45.	6.
32	50.33	1.8114	100.	13.
33	53.22	1.7196	87.	12.
34	53.85	1.7010	152.	20.
35	53.96	1.6978	152.	20.
36	54.85	1.6723	97.	13.
37	55.12	1.6648	88.	12.
38	55.53	1.6535	248.	33.

A set of curves was developed from which one particular process could be chosen in order to fabricate an 80% dense pellet. The matrices of a number of pellets were then characterized using a nitrogen permeability apparatus built at Semicon for this contract. Figure 3 (page 12) is a block diagram of the apparatus. The samples were thin pellets which had been etched to open the surface pores. They were then sealed and attached to the apparatus by way of shrinkable tubing that had a meltable inner lining. The seal was checked for pressure leaks with soapy water thus assuring that only the pellet face area was exposed to the diffusant gas. The other components of the system were a dry nitrogen supply with a pressure regulator, a solenoid valve, a gas chamber of known volume, a mercury manometer with attached electric eyes, and a digital stop clock. The clock timed the interval for the known volume of gas to undergo a given pressure decrement. Ten measurements were made for each sample. The mass permeability coefficient was then calculated from Carman's formula³.

CARMAN'S FORMULA:

$$K = (\delta m) \left(\frac{L}{A} \right) \left(\frac{1}{\delta t} \right) \left(\frac{1}{\Delta P_{mm}} \right), \text{ gm.cm}^{-1} \cdot \text{sec}^{-1} \cdot \text{mm Hg}^{-1}$$

where

$$\delta m = \frac{\delta P_{mm} \cdot V \cdot M}{RT}, \text{ gm of N}_2 \text{ diffusing in } \delta t \text{ seconds}$$

M = gm/mole, molecular weight of N₂

R = ideal gas constant

T = °K, absolute temperature

$\frac{L}{A}$ = cm⁻¹, length/area ratio of test sample

ΔP_{mm} = mmHg, mean differential between gas chamber and atmospheric pressures during δP_{mm} decrement

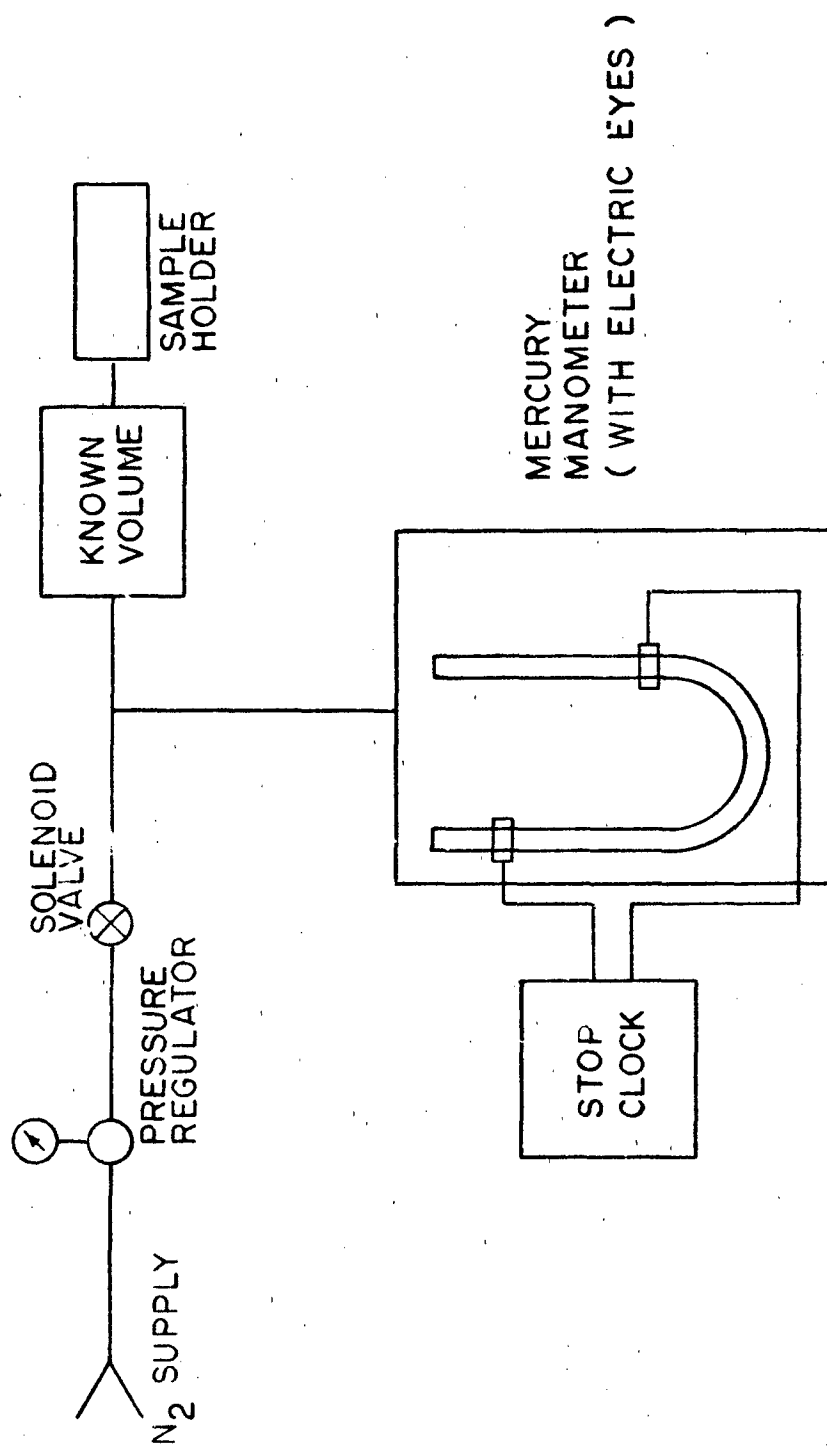


Fig. 3. Block Diagram of Nitrogen Permeability Apparatus

All permeability coefficients were determined using the following parameters:

$$\begin{aligned}M &= 28.02 \text{ gm mole}^{-1} \text{ N}_2 \\R &= 82.057 \text{ cm}^3 \text{ atm } ^\circ\text{K}^{-1} \text{ mole}^{-1} \\T &= 298 ^\circ\text{K} \\V &= 1000 \text{ cm}^3\end{aligned}$$

Scanning electron microscopy (SEM) was used to characterize the matrices. The surfaces were checked for general appearance and any smearing that may have occurred. Photographs were taken for comparison to a standard tungsten matrix.

The next step was to choose the correct parameters required to fabricate an 80% dense rhenium cathode. That essentially consisted of deciding upon the process that would provide a sintered pellet in a time approximately equal to that for tungsten pellet production which is one hour. The sintered pellet would then be impregnated with either 4:1:1 or 5:3:2 impregnants and then machined to tolerances of + or - .0005 inches. The configuration of the product was a simple cylinder .100 inches in diameter and .040 inches in length. That was then crimped into a molybdenum sleeve support assembly. For testing purposes each cathode was built into a close spaced diode within a glass envelope. Other components of the diode assembly were as follows:

1. A free-standing heater which is placed into the molybdenum sleeve.
2. A guard ring structure consisting of 2 pins supporting a molybdenum ring which is coplanar with the surface of the cathode. The guard ring and the cathode are attached to the same pins to eliminate spacing problems.
3. A molybdenum anode placed .020 inches above the surface of the cathode, and biased with a D.C. power supply.

The glass envelope was continuously pumped with a Varian 2 liter per second Vac-ion appendage pump. This was the sole pump after the cathode had been activated on a vacuum station that had reduced the pressure to a maximum of 1×10^{-6} torr. Figure 4 (page 14) is a sketch of the entire assembly minus the appendage pump.

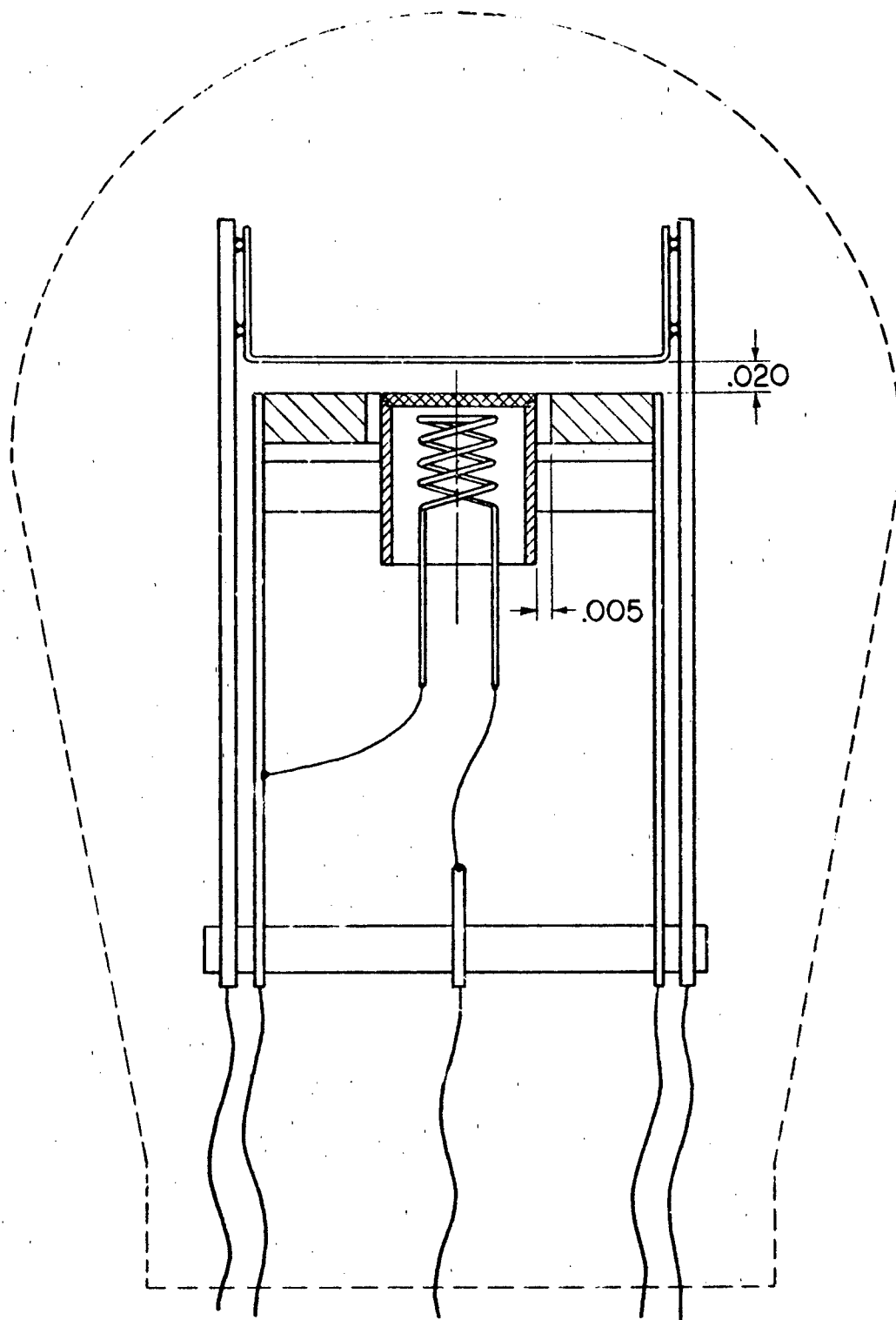


Fig. 4. Diode Assembly

After fabrication the diodes were subjected to accelerated life testing. This was initiated with the cathode activation procedure that is also used for Semicon's tungsten cathodes. The procedure is shown in Table 3 on page 16.

All pressures were measured with a hot filament ion gauge. The pressures listed are the final pressures at which the current stabilized before moving to the next step. These are not requirements but are, instead, measurements made from a typical activation. The "tip off" refers to sealing off the individual diode from the glass manifold. Each diode was then aged with dc voltage on the anode (0 to 200 volts) and periodically pulse-tested at high voltages using a Cober pulse generator at 60 pps and 5 μ s pulse width. A baseline of information was to be developed by running 2 diodes of each impregnant type at 2, 4, and 8 A/cm² at 250C above the knee temperature. These were then supposed to be compared to tungsten diodes of the same type, but it shall be discussed later why this was not the case.

5.0 RESULTS AND DISCUSSION

Due to the 6 to 7 micron average particle size requirement, the rhenium powder procurement was somewhat difficult. After contacting a number of possible vendors, it became evident that the tolerance needed to be changed. Eventually, Surepure Chemetals, Inc. was found to be able to supply 99.99% pure rhenium powder which had an average particle size of 4 to 8 microns. After its purchase, the powder was subjected to a number of physical characterizations. Particle size analysis revealed the average size was 6.8 microns with approximately 85% of the distribution occurring between 1 and 10 microns^a. A graph of the distribution can be seen in Figure 5 (page 17). As it turned out, the powder perfectly fulfilled the original size requirements. A chemical analysis for metallic impurities was supplied with the powder, but, for comparison, another analysis was performed.^b The second

a Performed by Micromeritics Instruments using a Sedigraph.

b Performed by National Spectrographic Laboratories using emission spectroscopy.

TABLE 3. CATHODE ACTIVATION PROCEDURE

	Typical Pressure (torr)
1. Bake out diodes	
2. Cathode 750°C + or - 25° for 3 minutes	2×10^{-6}
3. Cathode 925°C + or - 10° for 3 minutes	1×10^{-6}
4. Cathode 1000°C + or - 10° for 3 minutes	3×10^{-7}
5. Cathode 1000°C + or - 10° for 3 minutes, anode 30 volts	3×10^{-7}
6. Cathode 1050°C + or - 10° for 10 minutes, anode 50 volts	3×10^{-7}
7. Cathode 1100°C + or - 10° for 10 minutes, anode 75 volts	3×10^{-7}
8. Cathode 1050°C + or - 10° for 10 minutes, anode 100 volts	3×10^{-6}
9. Cathode 1050°C + or - 10° for 30 minutes, anode 150 volts	3×10^{-6}
10. Degas-Cathode 1050°C + or - 10° for 2 minutes, anode 150-200 volts	3×10^{-6}
11. Cathode 1050° + or - 5° for 10 minutes, anode 150 volts	3×10^{-7}
12. Cathode 1050° + or - 10° for 10 minutes, anode 100 volts	3×10^{-7}
13. Cathode 1100° + or - 5° for 10 minutes, anode 100 volts	3×10^{-7}
14. Tip off when pressure reaches 2×10^{-7}	

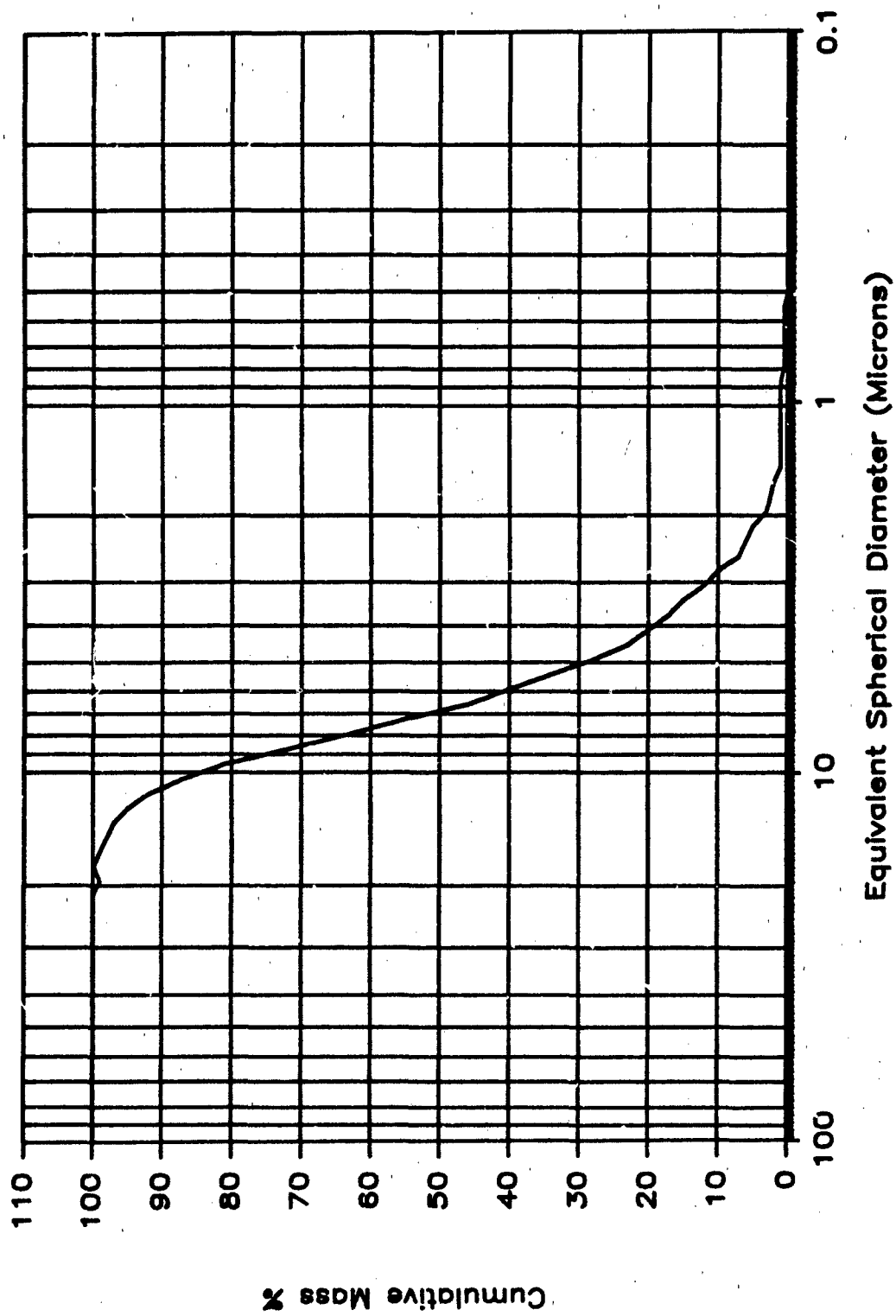


Fig. 5. Particle Size Distribution of As-Received Rhenium Powder

analysis also included analyses for carbon and sulfur content. Both sets of data can be seen in Table 4 (page 19). As expected, the powder purity was acceptable and there were no notable features.

5.1 Powder Characterization

Random samples of powder were analyzed with an ISI 60 Scanning Electron Microscope (SEM) for particle shape characterization. The general shape could be described as irregular spheroids and can be seen in Figure 6 (page 20).

The photographs are of typical samples viewed at 2000x. In an attempt to improve the shape regularity, a few samples of loose powder were heated at various temperatures to produce some agglomeration. It was found that powder sintered at 1600°C for 20 minutes would agglomerate into a solid mass which then had to be ground with a mortar and pestle. It is clear in the photographs of Figure 7 (page 21) that the particles had necked together, but it could not be concluded that the shapes were any more regular. The purpose for producing larger and more regular shape was to develop a powder that could be packed and sintered to a more uniformly porous matrix. This has been demonstrated by others in the field. The powder produced at Semicon in this manner was then delivered to the contract monitor.

With the knowledge that the rhenium necks together at 1600°C, a study of density versus pressing pressures, sintering temperatures, and sintering times was begun. The first study consisted of measuring the green densities of pellets as a function of their respective pressing pressures. Four samples each were pressed at 20, 30, and 50 kpsi and results are graphed in Figure 8 (page 22). A mean density for each pressure is shown. The density of 4.5 micron average size tungsten pressed at 20 kpsi is also shown for comparison purposes. As expected, the larger sized rhenium packed to a lower green density than tungsten for a given pressure.

These same pellets were then subjected to various sintering temperatures for 1 hour to obtain a sense of the rate of densification for various initial densities. The results are shown in Figure 9 (page 23). It is apparent that the densification rate is directly related to green density. This would be expected. Also, the degree of densification increased with temperature as expected.

TABLE 4. CHEMICAL ANALYSIS OF RHENIUM POWDER

Analysis Provided by Vendor

<u>Element</u>	<u>Quantity (ppm)</u>
Al	< 1.0
Ca	< 1.0
Cu	< 1.0
Fe	5.0
K	< 5.0
Mg	< 1.0
Mo	< 5.0
Na	< 5.0
Ni	5.0
Sr	< 5.0

Elements sought but not detected: Ag, B, Be, Bi, Cd, Co, Cr, Li, Mn, Nb, P, Pb, Sn, Ti, V, W, Zn, Nr, As, Sb, and Th.

Analysis Obtained by Semicon

<u>Element</u>	<u>Quantity (ppm)</u>
Ca	< 1.0
Fe	< 5.0
Mn	< 1.0
Na	< 1.0

Quantity (%)

C	0.010
S	0.004

Elements sought but not detected: Ag, Al, As, B, Ba, Be, Bi, Cb, Cd, Co, Cu, Ge, In, K, Li, Mg, Mo, Ni, Pb, Sb, Sn, Sr, Ti, V, W, Zn, and Zr.

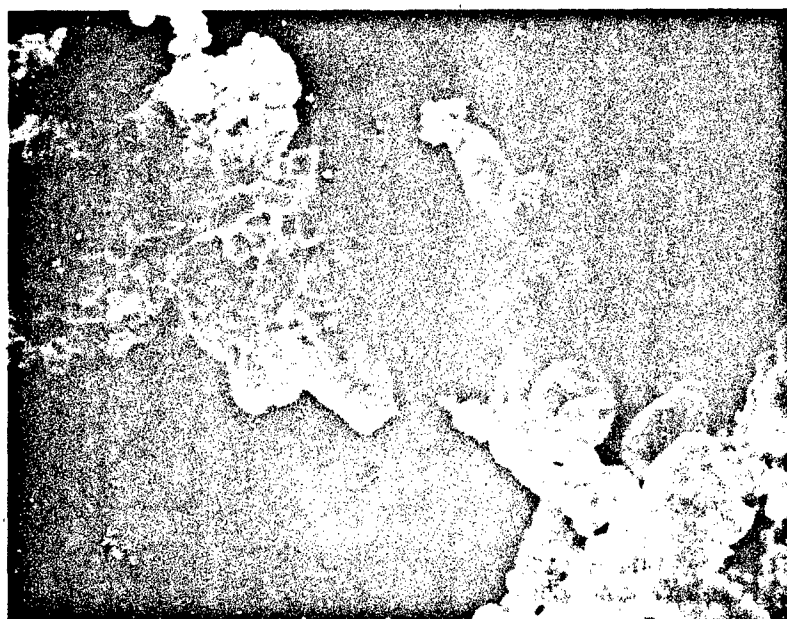
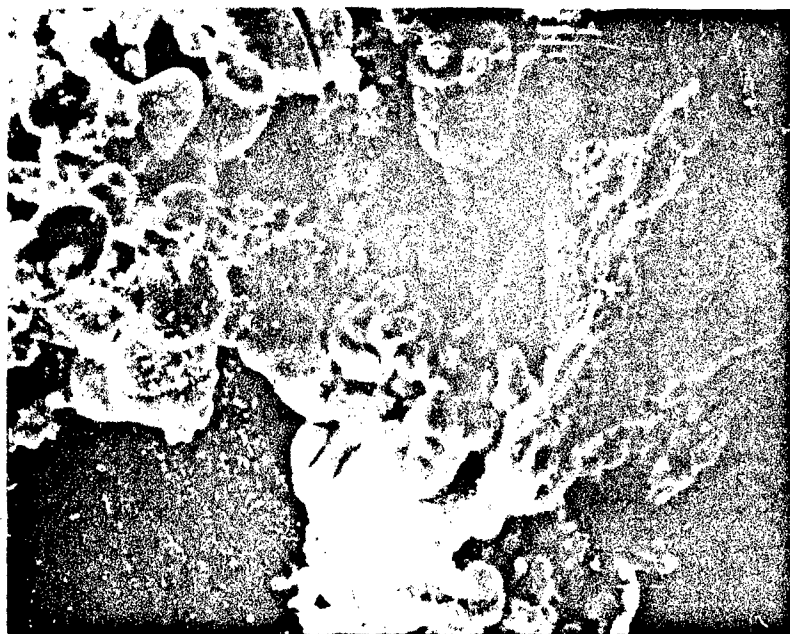
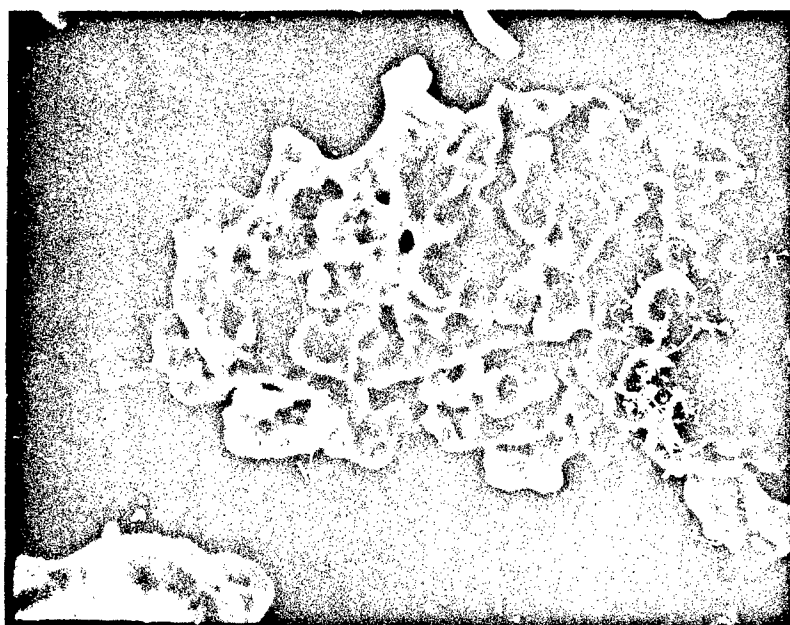
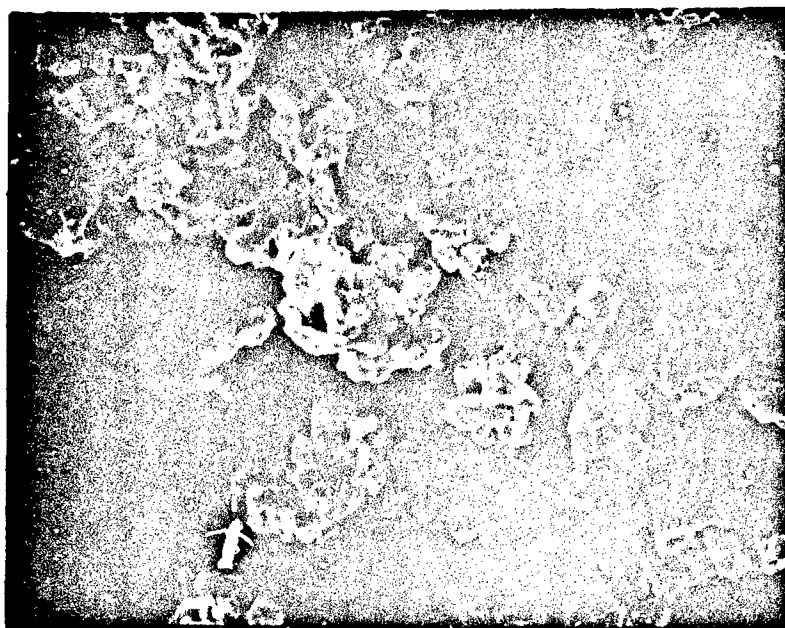


Fig. 6. SEM Micrographs (2000x) of As-Received Rhenium Powder



**Fig. 7. SEM Micrographs of Rhenium Powder after Agglomeration
by Heating to 1600°C for 20 Minutes
(Top: 1000x, bottom: 2500x)**

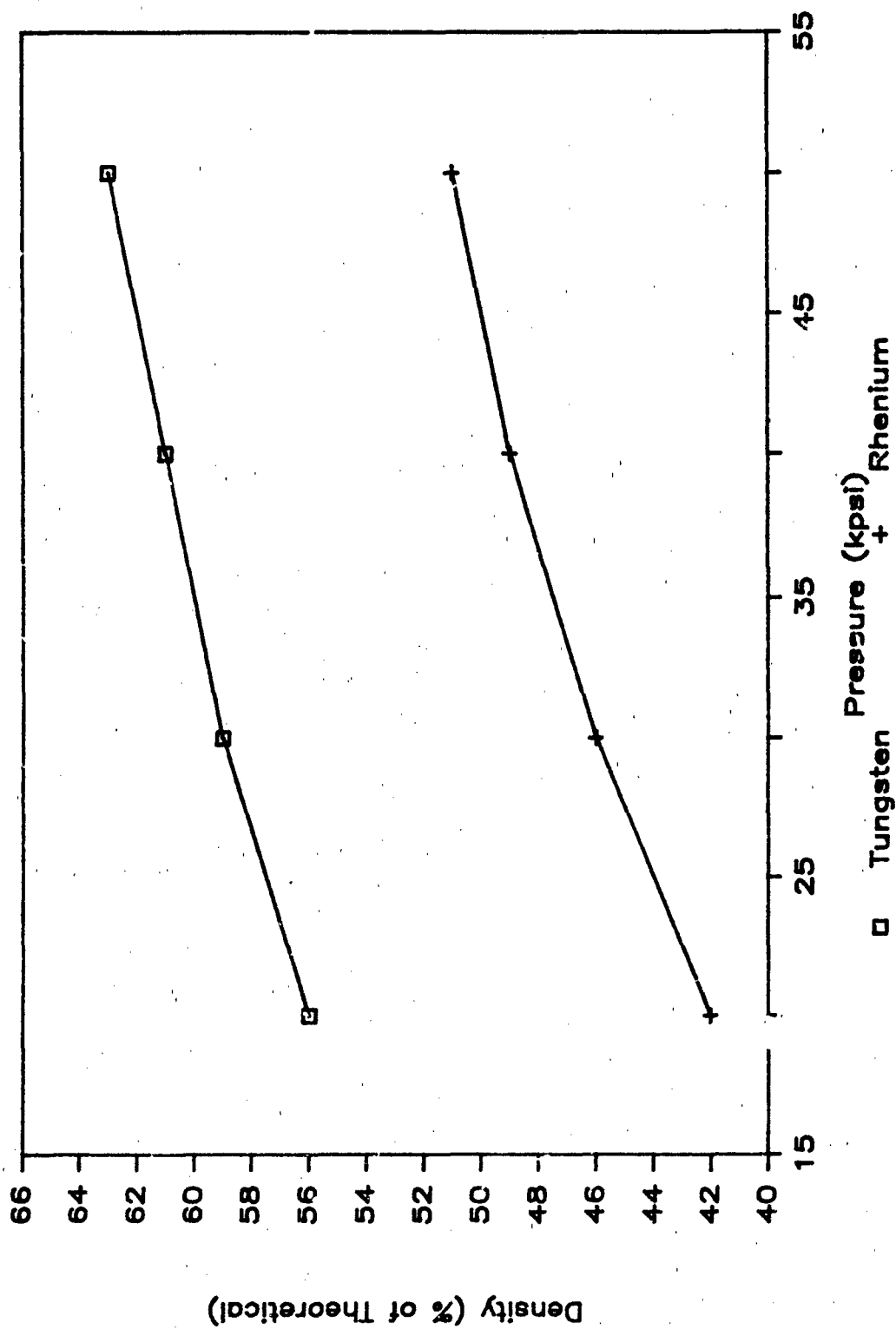


Fig. 8. Green Density versus Pressing Pressures

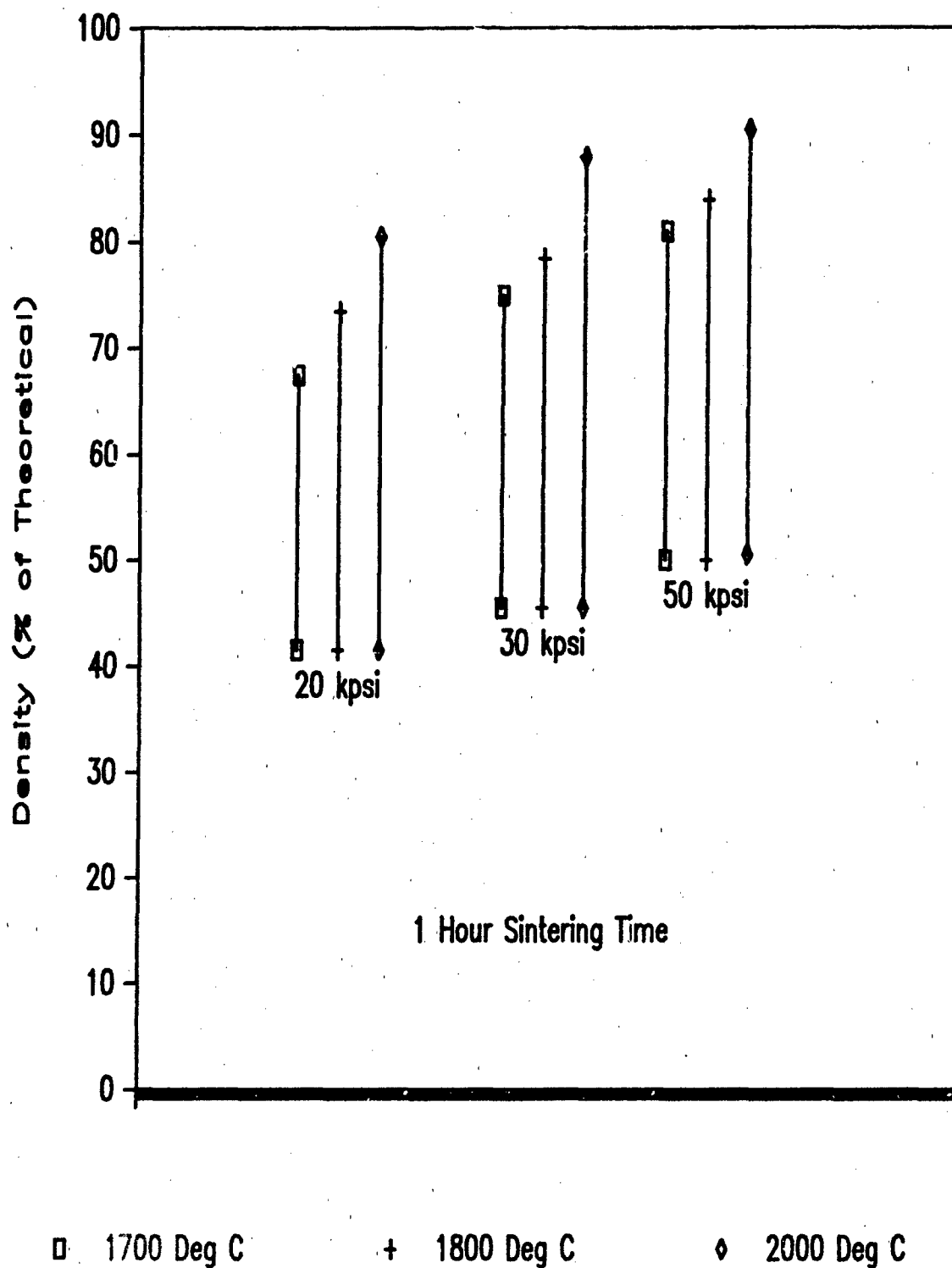


Fig. 9. Density of Rhenium Billets Pressed at 20, 30, and 50 kpsi Sintered for 1 Hour at Three Temperatures

To gain more insight into the sintering characteristics, additional pellets were pressed at 20, 30, 40, and 50 kpsi. Several of the pellets pressed at 20 kpsi crumbled. The remaining pellets were then sintered at temperatures from 1600°C to 2000°C for 10 minute increments. The results of these studies are shown in Figures 10 through 13 (pages 25 through 28). The most notable feature of the study was the rapid initial sintering rate of the rhenium.

The curves seem quite regular in shape, but the slope is much greater than expected for powdered tungsten. For comparison purposes, a 4.5 micron tungsten sinters from approximately 56% to 80% of theoretical density in 60 minutes at 2200°C. A rhenium pellet pressed to the same green density and sintered at 2200°C for 1 hour would be expected to attain over 90% of its theoretical density.

After developing the sintering curves, the next step was to develop an etchant to facilitate metallographic examination of the sintered pellets. Various etchants were tried, the best of which seemed to be an electrolytic etch with HCl as the electrolyte. A number of different pellets were etched and are shown in Figures 14 through 17 (pages 29 through 32) with a standard Semicon production tungsten bar for comparison. The tungsten bar was etched with Murakami's etchant. In general, the rhenium showed a smaller grain size with approximately the same density as the tungsten.

5.2 Cathode Fabrication

The next step in the program required a decision on a particular fabrication process to produce an 80% dense pellet, impregnate that pellet, and then machine it. A number of factors were considered such as the length of time of sintering, temperature, pressing pressure, pressing method, and machine chuck size requirements. Semicon's tungsten is cold isostatically pressed in a press with 30 kpsi capability so it would be simple to press rhenium in a like manner.

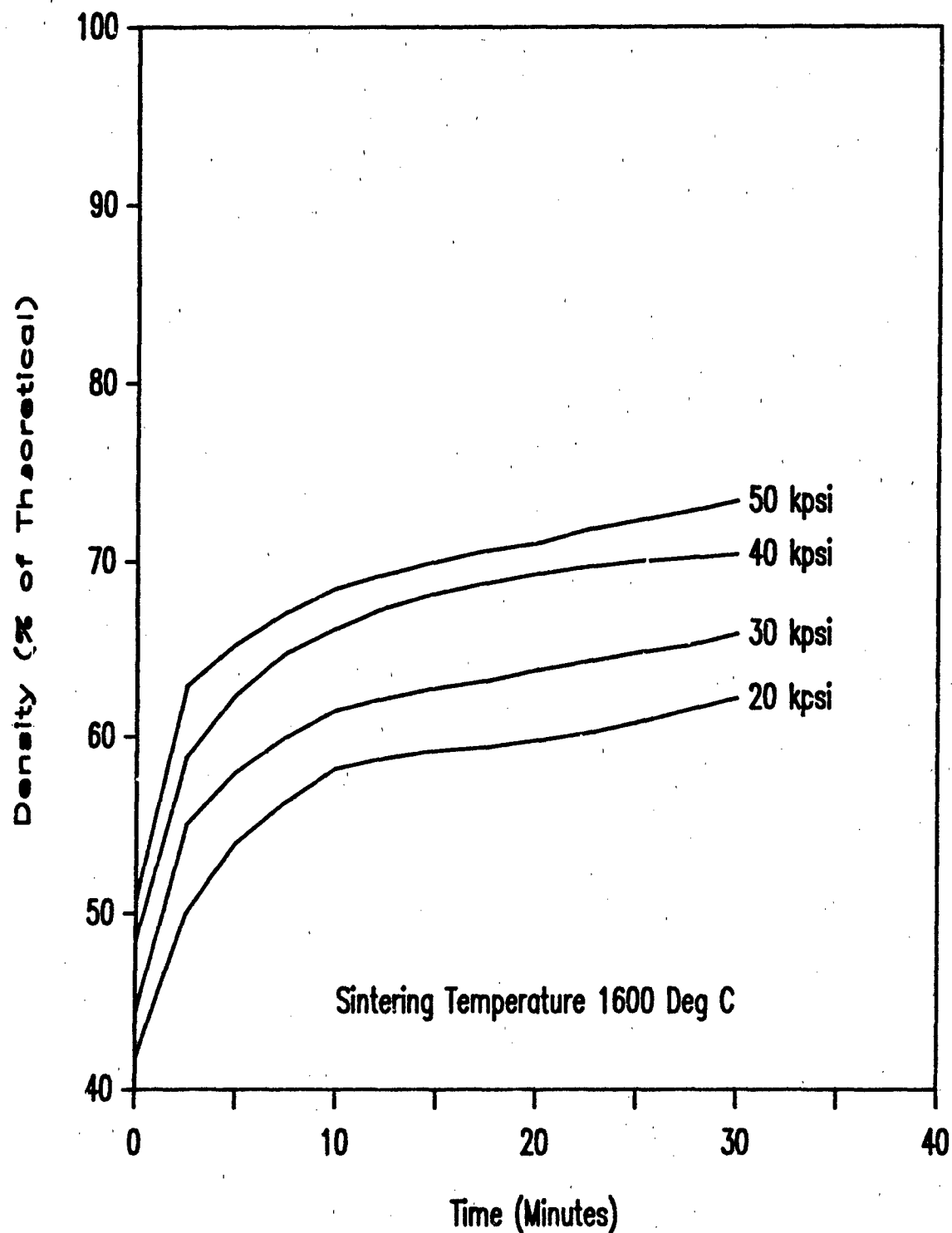


Fig. 10. Density of Rhenium Billets vs. Pressing Pressure and Sintering Time at 1600°C

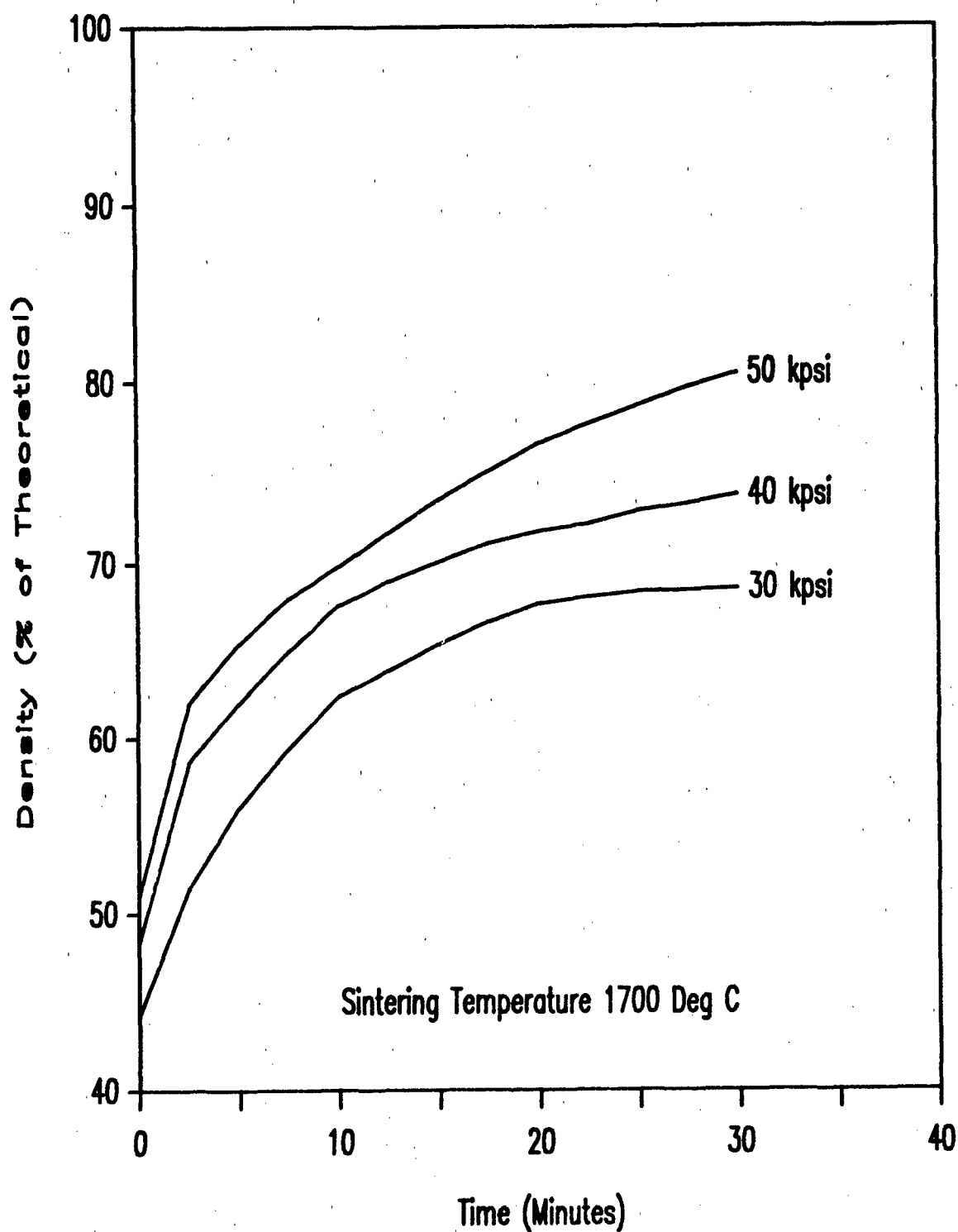


Fig. 11. Density of Rhenium Billets vs. Pressing Pressure and Sintering Time at 1700°C

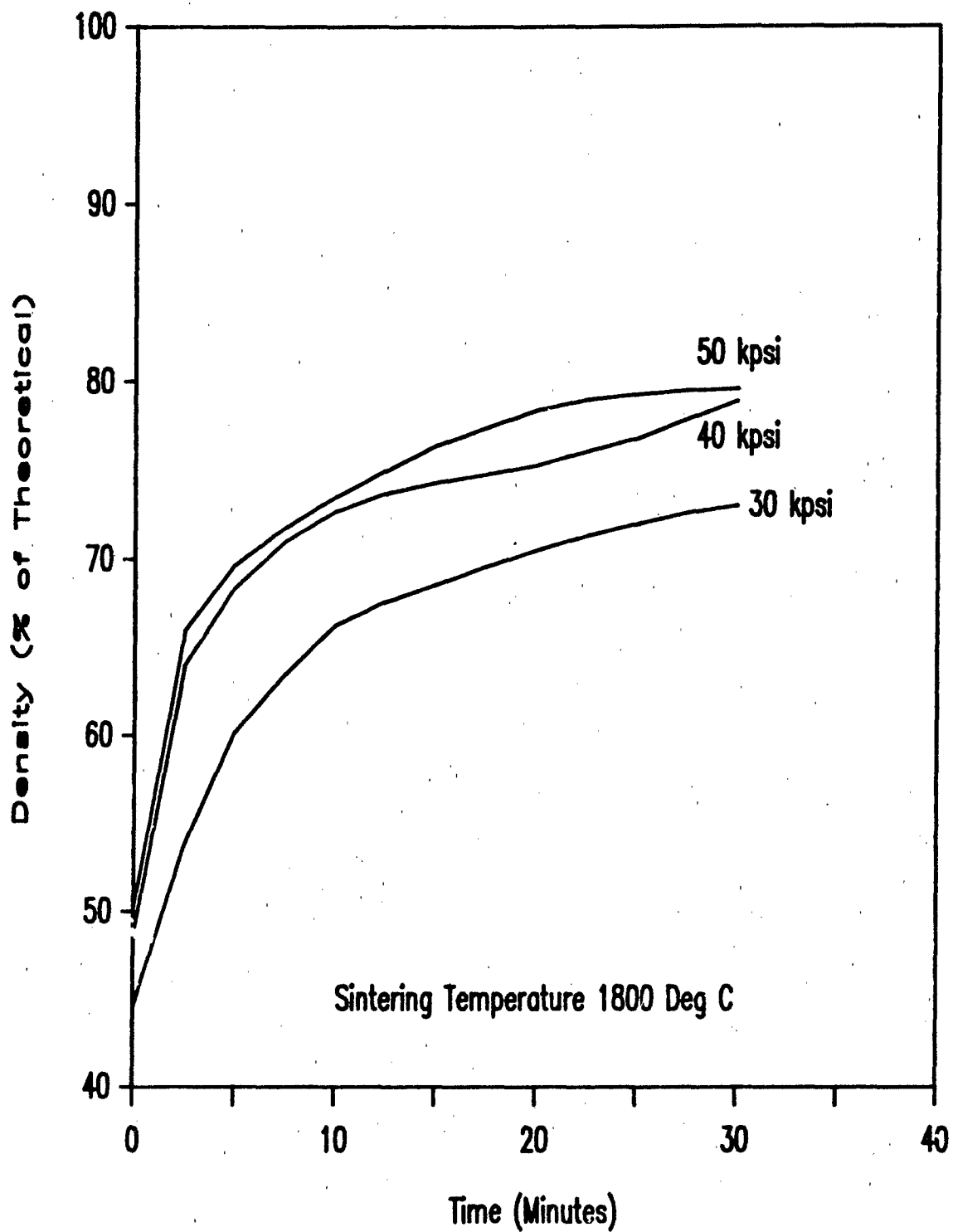


Fig. 12. Density of Rhenium Billets vs. Pressing Pressure and Sintering Time at 1800°C

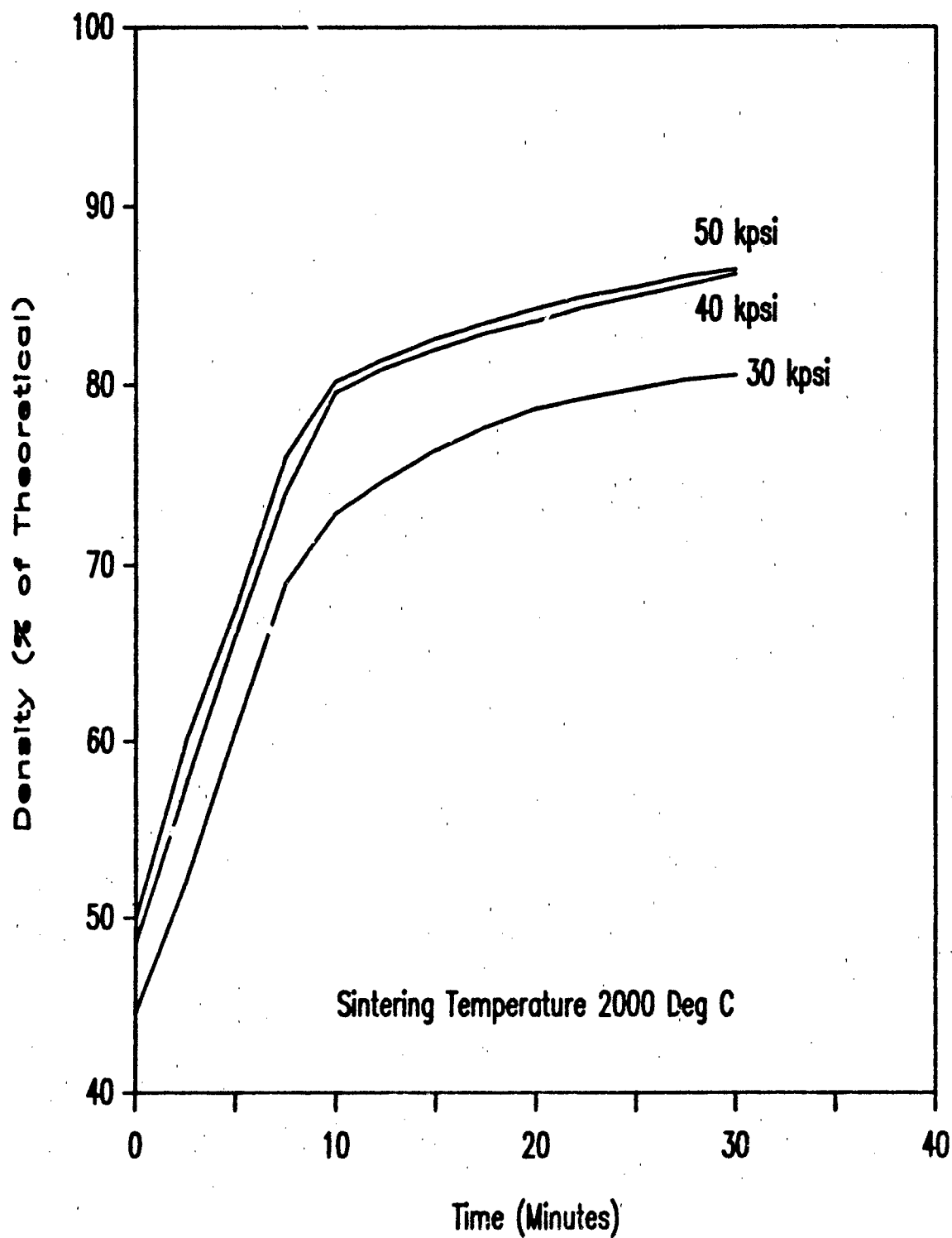


Fig. 13. Density of Rhenium Billets vs. Pressing Pressure and Sintering Time at 2000°C

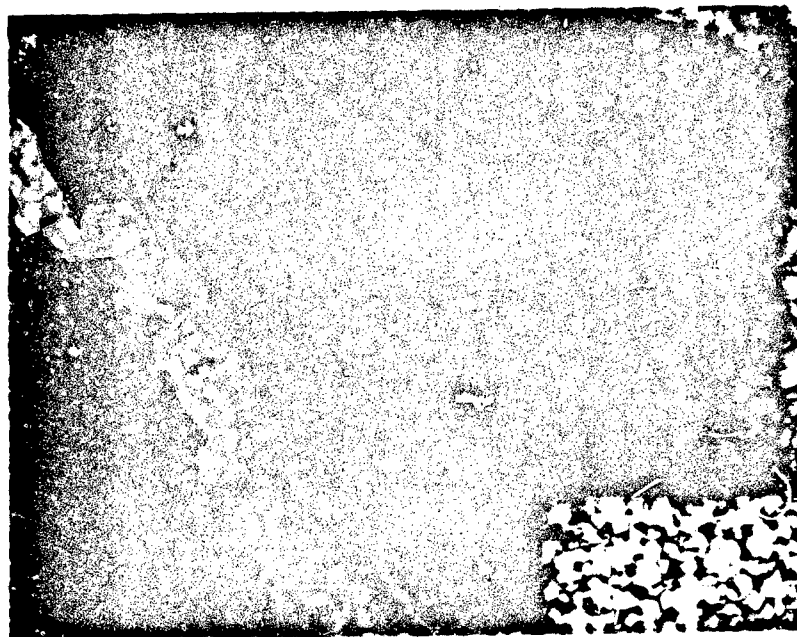


Fig. 14. Micrographs (500x) of a Standard Production Tungsten Bar (top) and a Rhenium Bar Etched with HNO_3 , Sintered at 2000°C for 1 Hour, 80.8% Dense (bottom)

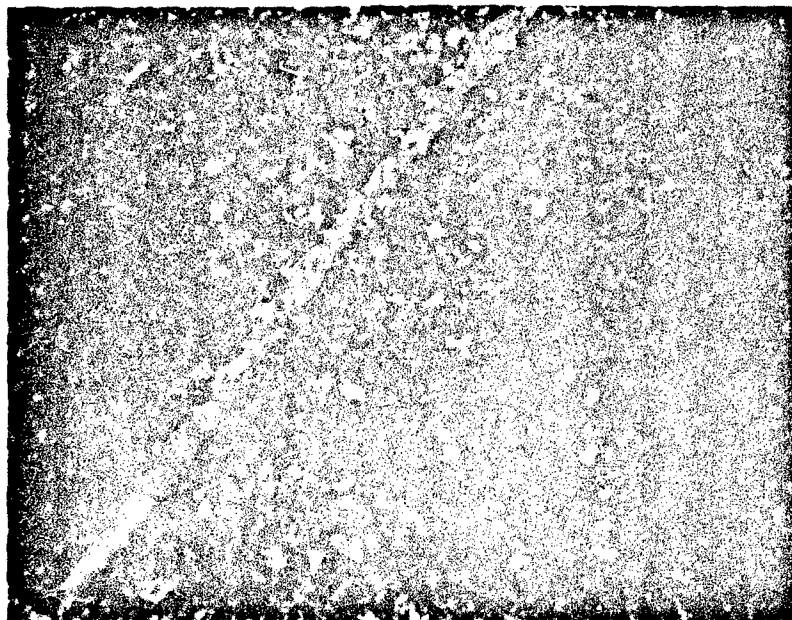
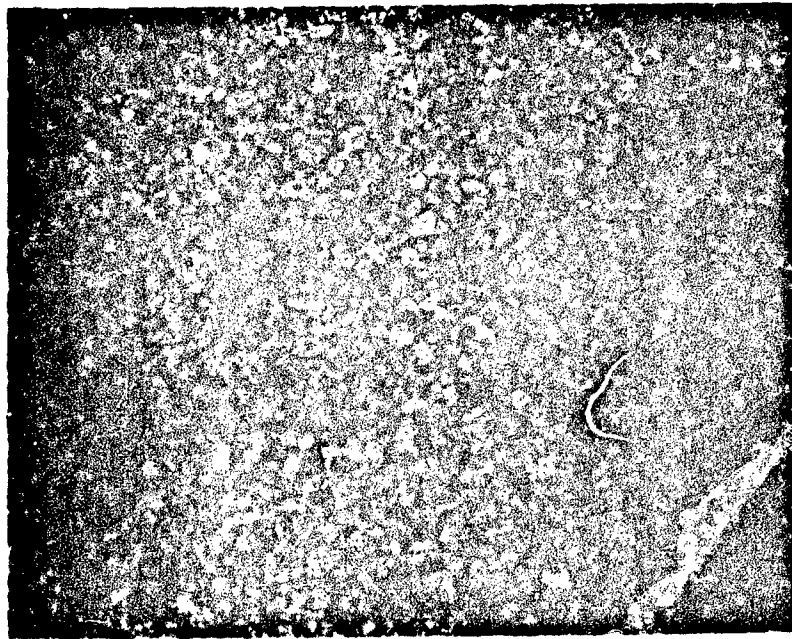


Fig. 15. Micrographs (500x) of Sintered Rhenium Bars Electrolytically Etched with HCl. Top: Pressed at 30 kpsi, Sintered at 1700°C for 1 Hour, 75% Dense. Bottom: Pressed at 50 kpsi, Sintered at 1700°C for 1 Hour, 81% Dense.

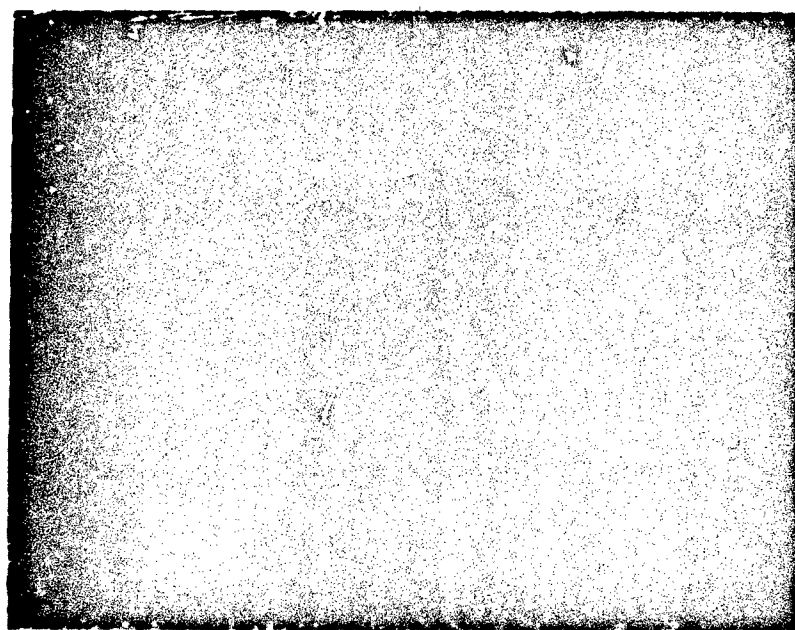
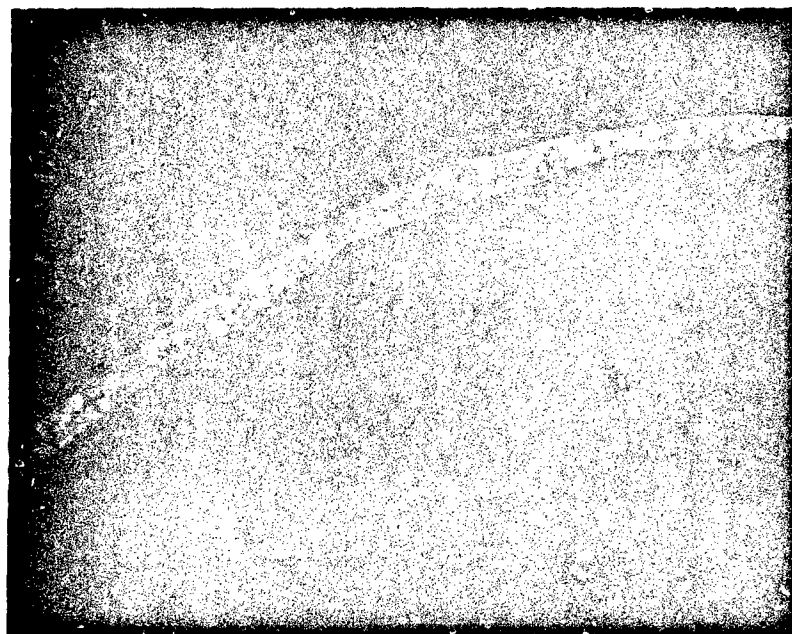


Fig. 16. Micrographs (500x) of Sintered Rhenium Bars Electrolytically Etched with HCl. Top: Pressed at 30 kpsi, Sintered at 1800°C for 1 Hour, 78.7% Dense. Bottom: Pressed at 50 kpsi, Sintered at 1800°C for 1 Hour, 84.1% Dense.

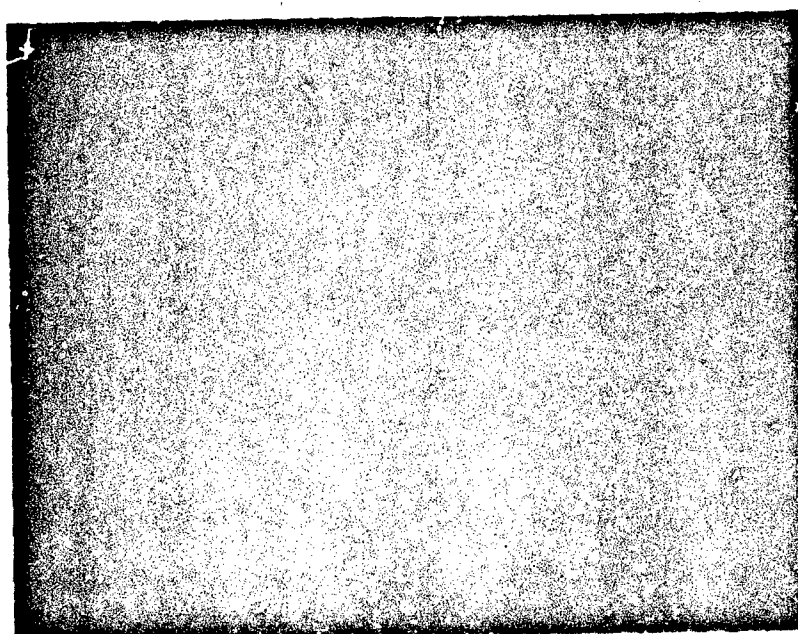
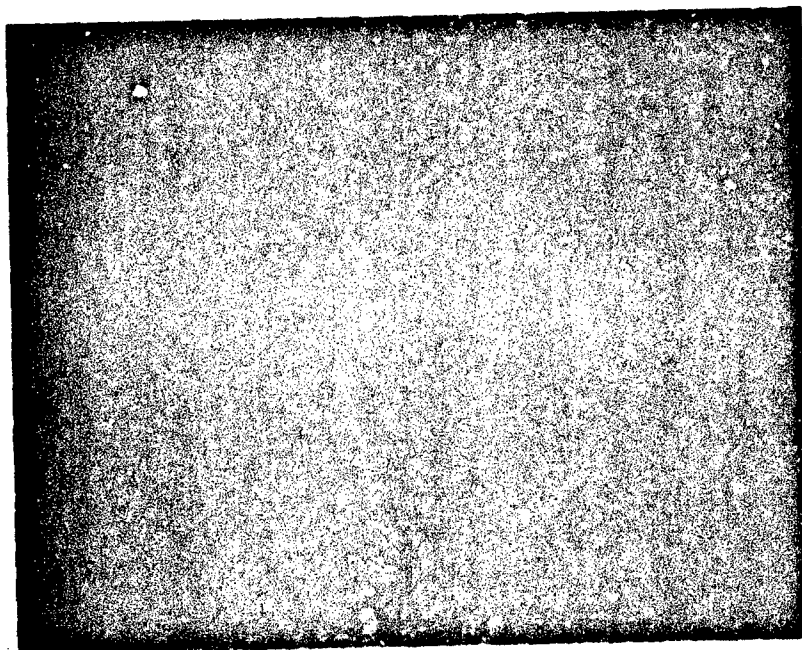


Fig. 17. Micrographs (500x) of Sintered Rhenium Bars Etched with HNO_3 . Top: Pressed at 30 kpsi, Sintered at 2000°C for 1 Hour, 88.3% Dense. Bottom: Pressed at 50 kpsi, Sintered at 2000°C for 1 Hour, 90.5% Dense.

An isostatically pressed bar would be long enough to be held in a machine chuck whereas a die-pressed pellet would not; so it was decided that isostatic pressing at 30 kpsi and sintering at 1800°C for 1 hour would produce the desired sample.

A bar, RB1, was processed this way and arrived at a density of 83% of theoretical which was greater than expected. The bar was divided into 2 pieces, one of which was impregnated with a 4:1:1 composition. This proved to be nearly impossible to machine. A point could not be held on the tool because of chipping, and there were complaints of extreme hardness of the material. The other piece of the bar was impregnated with methyl methacrylate for a lubricant and demonstrated machinability, although there were still complaints of extremely hard material. A study of the machined surfaces provided valuable information as to the cause of the difficulties. Figure 18 (page 34) contains two S.E.M. photographs of bar RB1 which show, conclusively, a great deal of surface smearing. The machinist also reported that the tool point was wearing away very quickly and that the material removed was in a granular form rather than chips or curls.

This information led to the following hypotheses:

1. In the case of the ceramic impregnated pellet, the tool was actually tearing through very tough rhenium matrix material until it contacted a much harder ceramic-filled pore. The shock would most likely be great enough to fracture a tool.
2. In the case of the plastic impregnated pellet, the tool was tearing material from the matrix which balled up and imbedded itself back into the surface to be cut. This process would eventually form a very tough and abrasive surface to be cut, a "rhenium grinding wheel" of sorts. Hence, the wear on the tool became excessive in a short time.

From photograph 1 shown in Figure 19 (page 35), it was obvious that the surface of a machined pellet would have insufficient porosity to provide an adequate barium supply. Consequently, it was decided that an etchant would be employed to remove any disturbed metal on the emitting surface. It consisted of 55% lactic acid, 27% nitric acid, and hydrofluoric acid made up the balance.⁴ After a number of trials, it was found that a soak of approximately 41 minutes would remove all disturbed metal. The photographs of Figure 19 clearly show the contrast between etched and unetched surfaces.

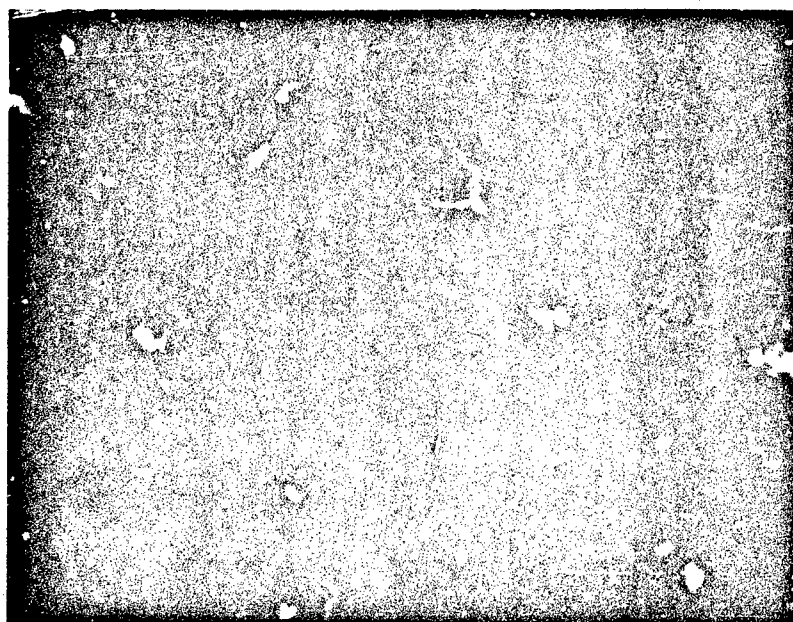
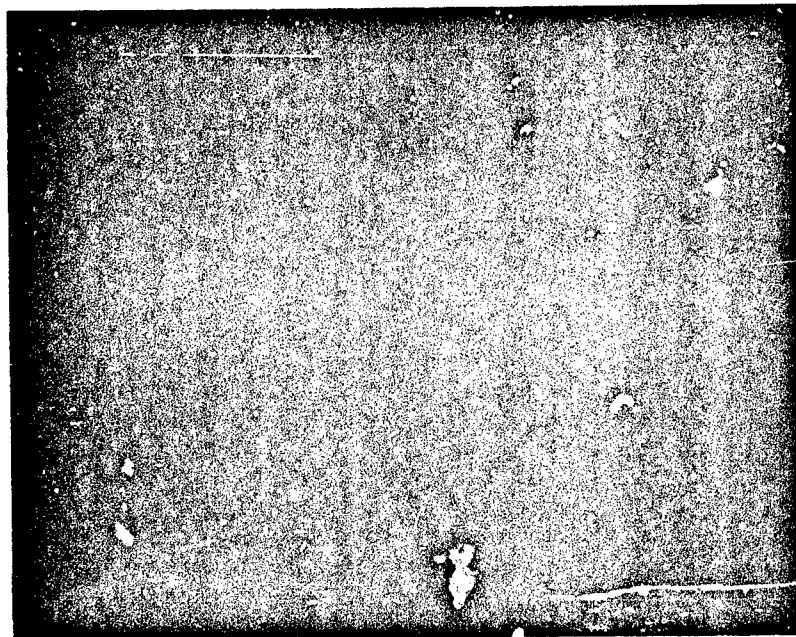


Fig. 18. SEM Micrographs (1000x) of 83% Dense Rhenium Bars after Machining. Top: Ceramic Impregnated. Bottom: Plastic Impregnated.

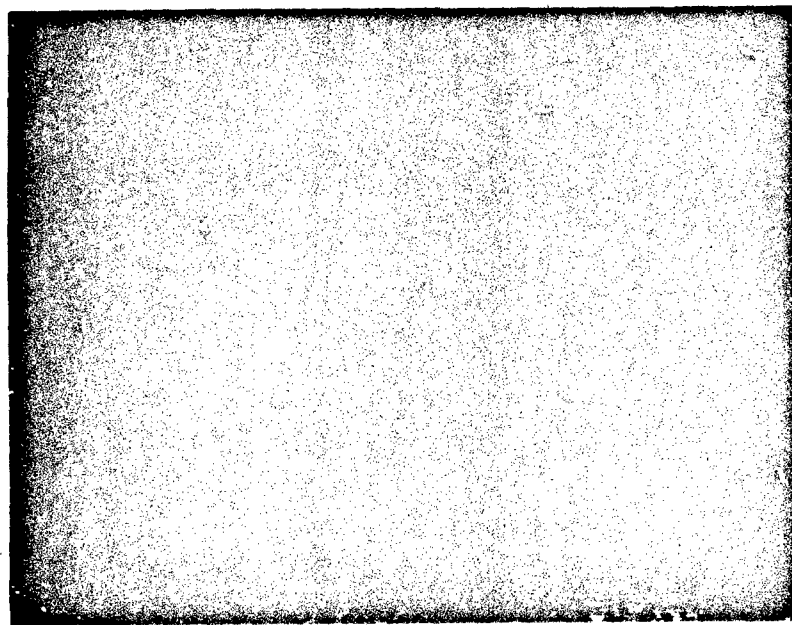
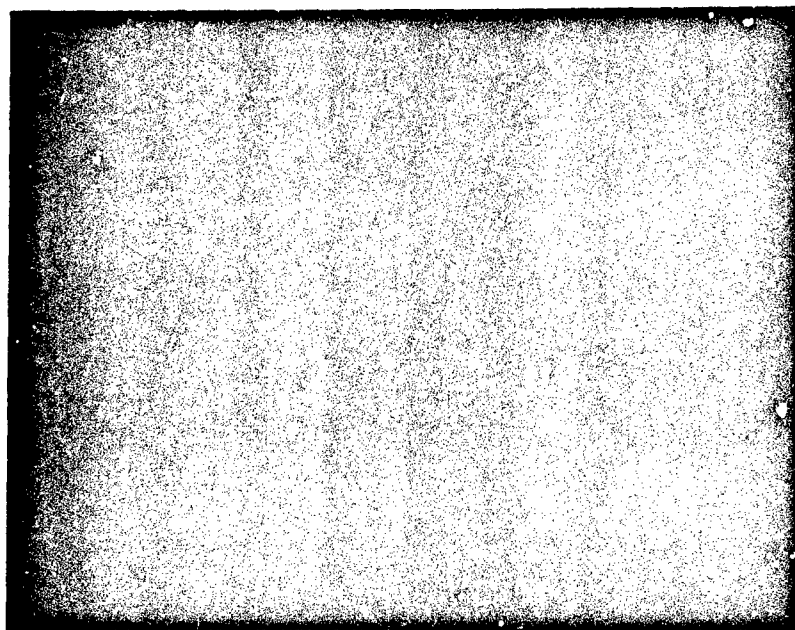


Fig. 19. SEM Micrographs (1000x) of Machined (65.9% Dense) Rhenium Pellets before Etching (top) and after Etching (bottom).

5.3 Permeability Testing

The finding of a suitable etchant also facilitated the permeability testing. An unetched, smeared surface would have precluded the possibility of any accurate data. Therefore, all rhenium samples were etched to open the surface pores. Two sets of samples were tested; one set of tungsten pellets and the other rhenium. A range of densities from 72% to 82% was chosen as the area of interest. All tungsten samples were also etched to preclude any inaccuracies attributable to surface smearing. The results indicate that the nitrogen mass permeability was a function of the material density and particle size. The tungsten powder with its smaller particle size would be expected to produce a slightly more permeable sample at a given density. It was also interesting to note that the procedure used to attain an 80% dense sample had little effect on the permeability. The results are shown in Figure 20 (page 37).

5.4 Emission Testing

As mentioned previously, the rhenium diodes were first activated in the same manner as a standard tungsten diode and then tested for emission performance. The activation procedure has been described, but one quickly realizes the process should be different for the two materials. A number of the rhenium diodes had to be eliminated due to zero emission during activation. All cathodes impregnated with 5:3:2 fell into this category. Figure 21 (page 38) shows a typical curve of emission performance produced by a tungsten diode which was operated at a temperature of 1050°C Brightness with various pulsed voltages on the anode. It should be noted that the current densities measured ranged from 1 to 30 A/cm². This is compared to a rhenium cathode tested under similar conditions. That cathode, RPE2-2, when tested at 1050°C, produced current densities measured between .06 and .70 A/cm². The attendant curve can be seen in Figure 22 (page 39). A number of spurious increases in emission occurred but could not be measured due to their transient nature. Essentially, the rhenium cathodes could be described as low or non-emitters when tested within these constraints.

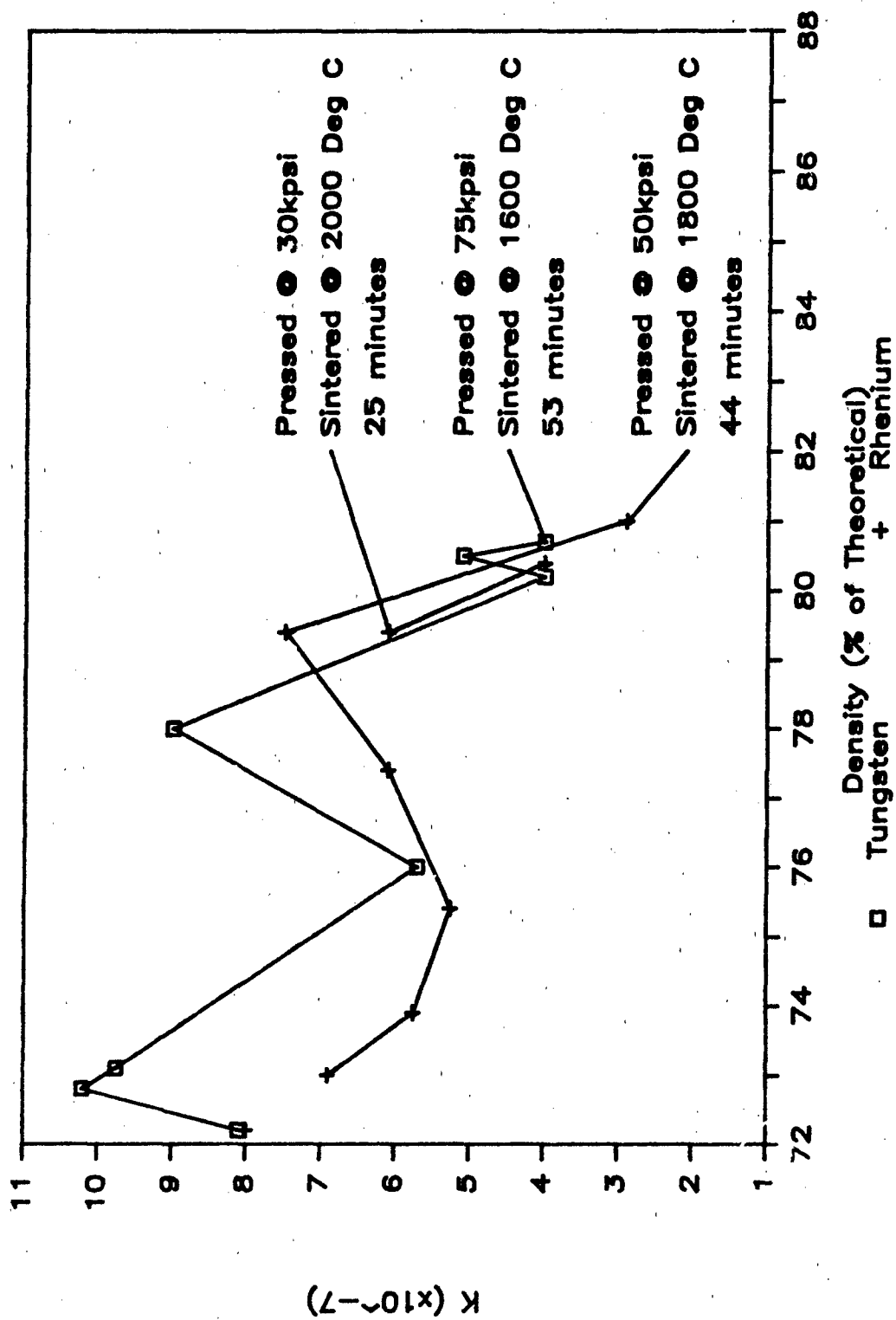


Fig. 20. Nitrogen Permeability of Tungsten and Rhenium Pellets vs. Density

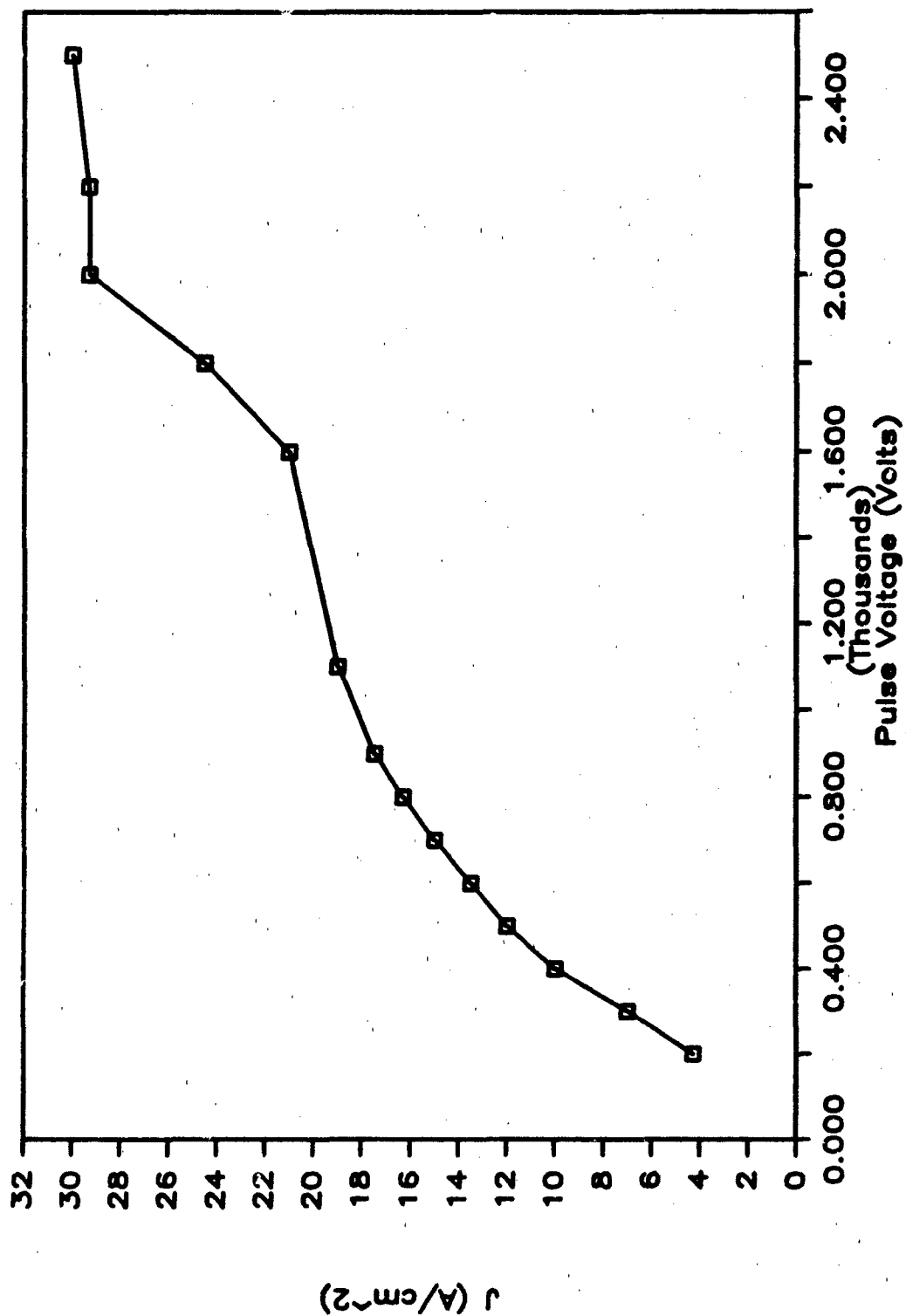


Fig. 21. Electron Emission of Typical Tungsten Cathode at 1050°C Br

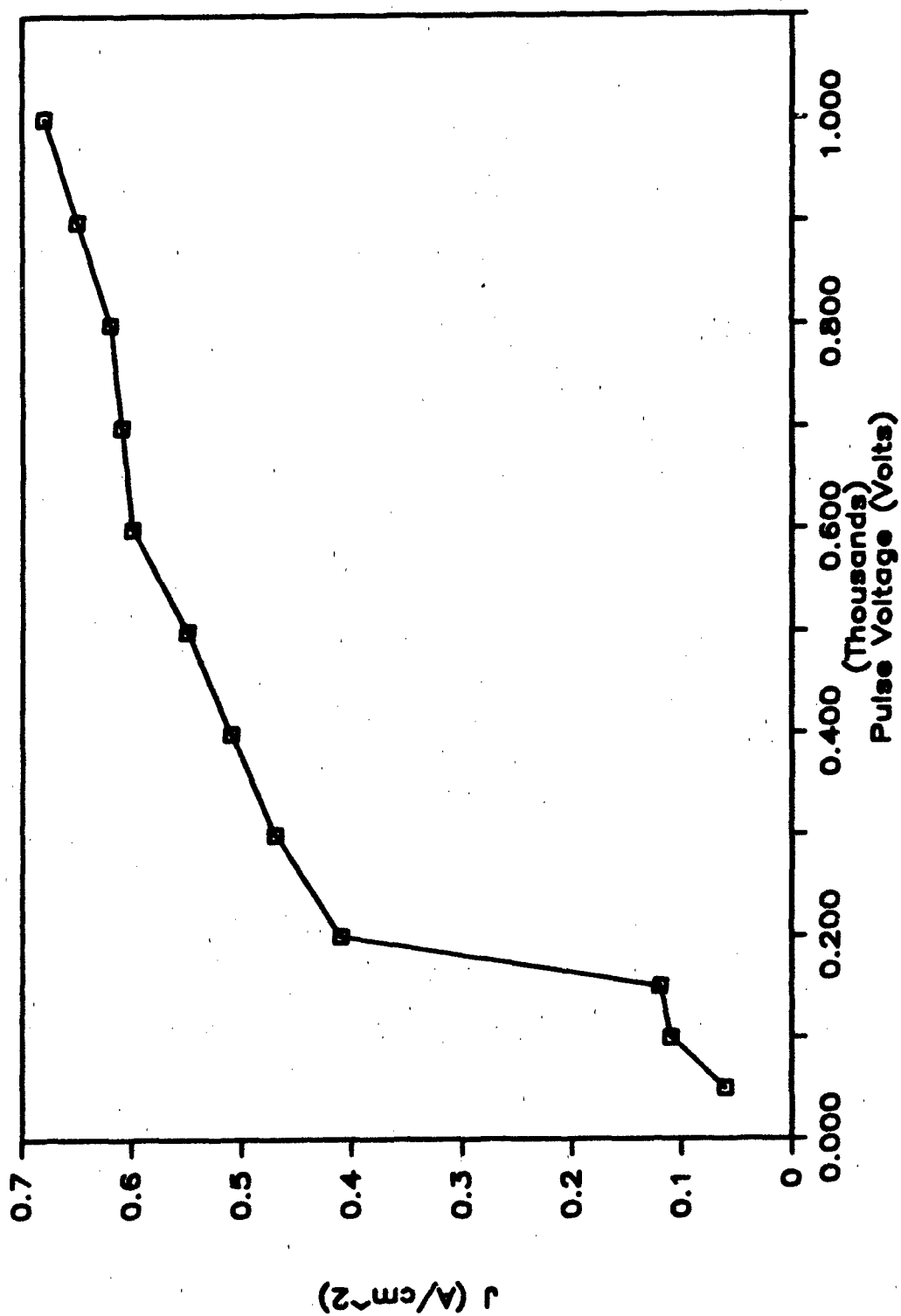


Fig. 22. Electron Emission of a Rhenium Cathode at 1050°CBr

However, one exception produced significant doubt in these test results. Earlier in this study, during fabrication studies, a bar had been fabricated and machined into cathode pellets of a comparable design. This bar was known as RB1. A sample pellet was impregnated with 4:1:1 and was labeled RB2A. It differed from the cathodes required for the contract in two ways. It had a diameter of .120 inches rather than .100 inches, and it had a slight spherical radius machined into the emitting surface. The cathode was then fabricated into a diode identical to that previously described. Since it was a different design and a preliminary test, the activation procedure previously presented was not adhered to. The diode was successfully tested and results are shown in Figure 23 (page 41). Based on these results, the rhenium cathode performed at least comparably to tungsten cathodes. The inconsistency in results led to a check of vacuum conditions, cleanliness of parts, and processing of the test diodes. The evidence indicated that the performance was being improved in the latter case due to the activation procedure employed. This led to an effort not called for by the contract.

Two cathodes were tested for evaporation rate by line of sight residual gas analysis (RGA) in the hope that light could be shed on the emission data. Although the results from these tests are recognized as being very limited, they led to a formal re-test of one diode.

It would have been preferable to reprocess and re-test all rhenium cathodes, but a lack of time precluded that possibility. The diode that was tested showed a drastic improvement in emission performance which could be described as highly encouraging. Continuous wave (CW) testing was utilized for comparison purposes. Current densities were measured as a function of the cathode temperature. Anode voltages of 100, 150, and 200 volts were used so a set of three curves is shown for each; the reprocessed rhenium cathode and a tungsten cathode in Figure 24 (page 42).

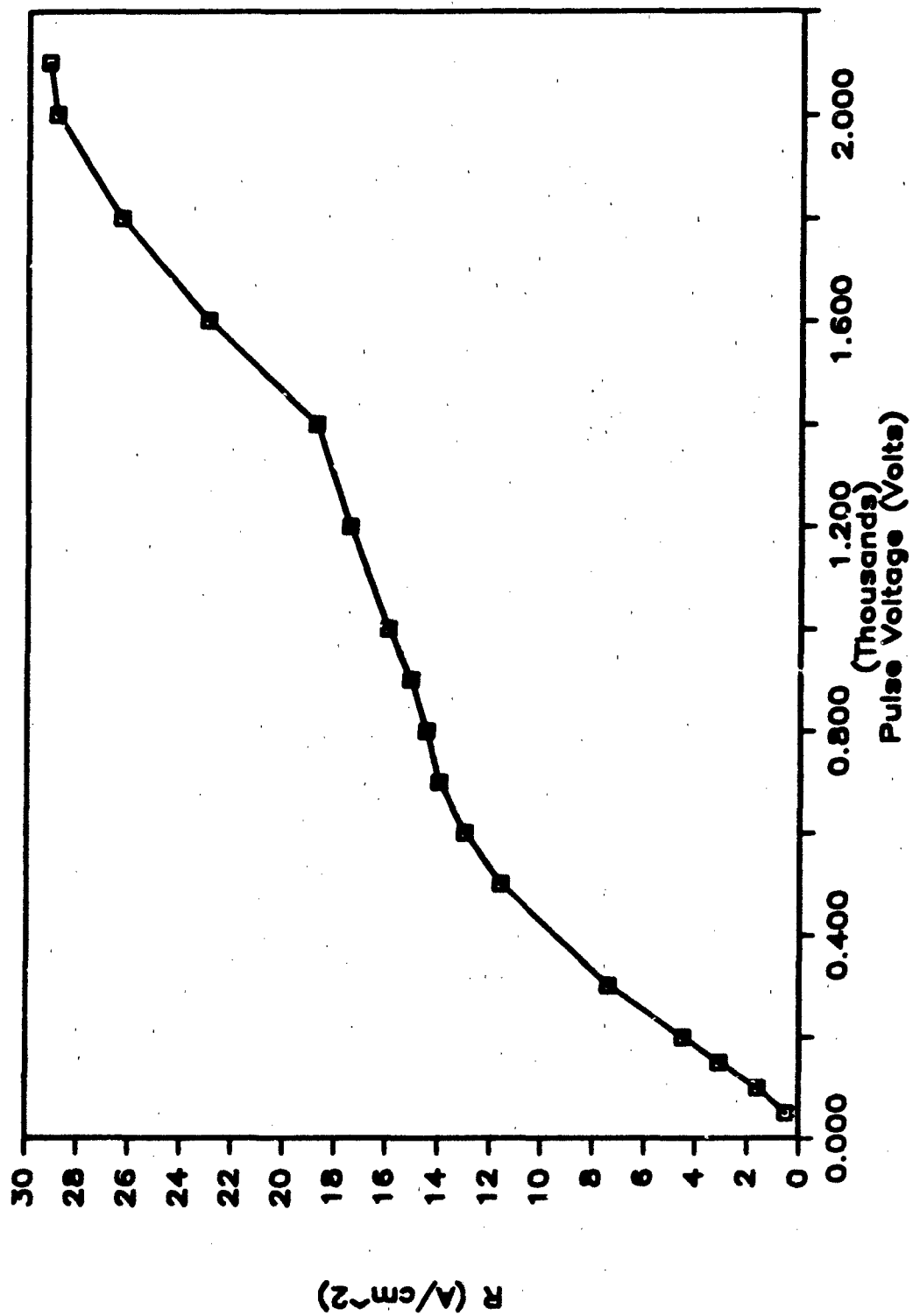


Fig. 23. Electron Emission of Rhenium Pellet RB2A at 1050°C_{Br}

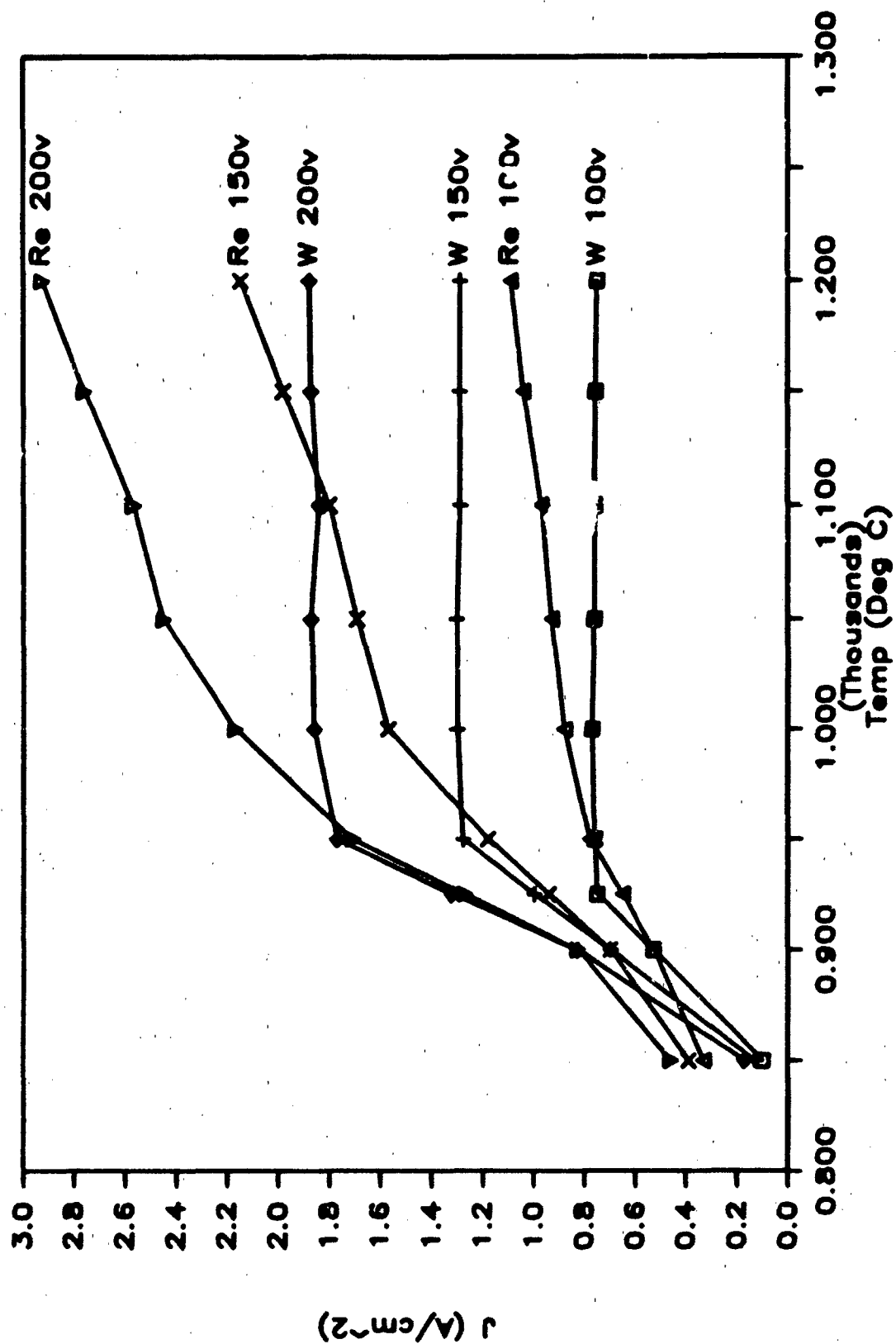


Fig. 24. Electron Emission of Typical Tungsten and Re-Processed Rhenium Cathodes

6.6 CONCLUSIONS AND RECOMMENDATIONS

The results of this program have demonstrated that rhenium powder can be fabricated into an emitting dispenser cathode. The processes involved are not too unlike those of tungsten. Machining of a sintered matrix causes difficulties with surface smearing, but those can be addressed by a simple etching procedure.

It was found that pulse testing rhenium cathodes did not always give an accurate measure of their capabilities. The authors feel that this may have been related to low matrix-impregnant reactivity and/or incomplete activation.

Further work produced evidence that a rhenium cathode can exhibit comparable or better emission performance than a tungsten cathode provided the activation procedure is adjusted for the rhenium cathode.

It should be recognized that the focus of the program was on the fabrication of a rhenium cathode. Further work needs to be done in the area of emission testing in light of the promising results produced here.

7.6 RECOMMENDATIONS FOR FUTURE WORK

- A. Further investigation of the activation procedure for a rhenium cathode to optimize performance.
- B. Study the cathode operation parameters to determine those conducive to superior performance.
- C. Investigation into the engineering of impregnants to fit the particular matrix and application.
- D. Study the feasibility of other cathode configurations, such as utilizing a porous rhenium plug in an L-type cathode.

BIBLIOGRAPHY

1. T. Hata and J. Kai, "Impregnated Cathode", Mitsubishi Denki Laboratory Reports, Vol. 4, No. 2, April 1983.
2. T. Hata and M. Koitobashi, "A Study of Molded Rhenium Cathode", Mitsubishi Denki Laboratory Reports, Vol. 5, No. 2, April 1964.
3. Carman, P.C., Flow of Gases Through Porous Media, Butterworth, London, 1949.
4. American Society for Testing and Materials, Annual Book of ASTM Standards, Part 11, ASTM, 1975.