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FINAL REPORT

VACUUM SPUTTERING PROCESS FOR CHROMIUM PLATING TITANIUM ALLOYS
PHASE II

U.S. Army Weapons Command
Rock Island Arsenal
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BY

T. Matley
R.T. Luedeman

Weston Instruments, Inc.
Weston -Newark
Newark, New Jersey 07114

20061018002

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SUMMARY

Feasibility of electroplating chromium onto titanium was demonstrated in an earlier effort. This was accomplished through the use of glow discharge sputtering techniques. Previous work using panels demonstrated the use of these techniques to clean titanium and sputter cover with chromium. These panels were then electroplated.

The sputtering apparatus was modified to prepare rod samples suitable for spin testing. Rods were prepared using alpha and alpha-beta titanium. Beta titanium was not used because the material could not be obtained.

Sputter rates were tested and variations in sputter methods were tried. Tests were made including spin testing for adhesion. The spin testing of the titanium rods and the steel control rods were done by W.H. Dancy, Jr. of the University of Virginia, according to the method outlined in his report EP 4424-105-61U.

A sample piece of hardware was successfully processed and an outline prepared, that is suitable for use as a process procedure. → [illegible]

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SECTION I - SCOPE

The scope of this work on a best effort basis was as follows:

1. To modify, as necessary, the sputter apparatus to accomplish sputter cleaning and sputter deposition of metal as a preparation for electroplating on cylindrical test specimens as well as flat panels.

Ti Cr Cr

2. To determine adhesion values of sputtered intermediate coatings utilizing the spinning rotor technique to determine optimum coating cycle.

3. To check hardness and microstructure of the sputtered coatings.

4. To work with alpha-titanium initially, then with alpha-beta and beta if available.

5. To evaluate adhesion of the system of electroplated chromium, over sputtered chromium over titanium. Comparison of these values to those of electroplated chromium on steel.

Cr, Ti

6. To determine the rate of formation of the sputtered metal layer.

7. To compare sputtered layers formed at fast and slow rates and evaluate for microstructure and hardness.

8. To note any effect (interstitial) on microstructure and hardness when sputtering is done with a small amount of hydrogen mixed with the argon gas for sputtering.

9. Investigation of methods of applying the process to small titanium hardware components on a production basis and prepare a production procedure for the process. pr

SECTION II - FOREWORD

Interest has been shown in obtaining a chromium electroplate over a titanium substrate. This suggests an attractive combination of properties that justify that interest. Because titanium is an extremely reactive metal, great difficulty has been encountered in attempts to electroplate using conventional methods. The sputtering technique described herein has produced results, when evaluated by spin testing, superior to any other known method.

In general, the vacuum sputtering technique removes material from the surface of a cathode. This is done in a vacuum bell jar using in this case, a partial pressure of pure argon. A high voltage is fixed across an anode and cathode within the bell jar. The gas molecules become ionized in the discharge and they move toward the cathode and arrive with an energy proportional to the potential difference between the anode and cathode. This kinetic energy of collision of the ionized gas atoms with the cathode atoms, is responsible for the subsequent expulsion of cathode material. Control of the process is by the voltage and the electrical current, a function of the partial gas pressure. The titanium is made the cathode and is thoroughly cleaned in the glow discharge. A switching arrangement permits immediate sputtering of a chromium cathode. The relative positions of the anode, titanium specimen, and chromium cathode results in deposition of chromium onto the ultra clean surface of the titanium. A useful thickness of sputtered chromium appears to be in a range of a few tenths of a micron up to 1 micron. Once the titanium substrates have been reduced to pure metal by cathodic

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SECTION II - CONTINUED

sputtering and the desired intermediate layer of chromium applied, then the specimen can be safely withdrawn from the inert atmosphere of the vacuum bell jar and the required chromium thickness applied by electroplating.

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SECTION III - PROCESS

This outline is suitable for use as a production procedure.

PROCESS A - Chemical Cleaning

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The initial operation is a chemical cleaning of the titanium to remove surface soil. Because hydrofluoric acid is used, all containers or measuring devices should be suitable for use with this acid (polyethylene, teflon, etc.). Size of the containers, amount of cleaning solution and other variables must be determined individually for each shape and size of component to be processed. The sequence of cleaning details is as follows:

1. Degrease
2. Acid Clean
3. Water Rinse
4. Alcohol and/or Acetone Rinse

Details

1. Degrease specimen by washing with C.P. Acetone. (In cases of more severe soil, this step may be preceded by conventional plate cleaning methods such as alkaline cleaning, ultra sonic cleaning in detergent solutions, vapor degreasing, etc.).

2. Typical Acid cleaning formulation:

Water	2 parts
Nitric Acid (conc. sp. g. 1.4)	5 parts
Hydrofluoric Acid (conc. 49%)	1 - 2 parts

Mix well-use in hood

Pour acid over the specimen using enough so that it is completely covered. Any exposed portion will darken due to the combination of heat, fumes and atmosphere.

If the solution has been well mixed, the cleaning will start uniformly allowing for the accurate timing of the cleaning with a stop watch. Substantial stock removal may result so proper care must be exercised if dimensions are very critical. Typical stock removal on a 1" X 3" alpha panel using approximately 25 ml of the above solution is as follows:

20 seconds	1.5 mil per side
40 seconds	2.5 mil per side
60 seconds	3.5 mil per side

The removal rate slows down rapidly as the acid in the solution is depleted so if close control of the removal rate is required, care must be exercised to use only the minimum amount of acid solution to cover the specimen and/or adjust the acid content downward to slow down the removal rate. Only a fraction of a mil need be removed in order to obtain a clean bright surface. Because the specimen will normally be electroplated with chromium in a subsequent operation, consider the build up effect of the electroplate on the final dimension along with this acid removal. Dimensional changes due to sputter cleaning and sputter deposition may be disregarded as their effects are measured in microns or less.

To stop the action of the acid solution, flood the acid solution with cool water.

SECTION III - PROCESS A CONTINUED

Allow the water to flow so that the container over flows, or decant while adding water to cool the part and dilute the acid. Keep the specimen covered with solution until cool.

3. Continue to rinse with water and finally rinse well with distilled or deionized water.

4. Rinse with C.P. Alcohol and C.P. Acetone to facilitate drying. (In large volumes, it may be possible to substitute warm air or another conventional method at this step.)

PROCESS B - Sputter Apparatus

The vacuum sputtering apparatus that is used is a conventional system modified slightly for this application.

The sputter system utilizes a typical 15 inch bell jar modified as shown in Figure 1. → p8

The three feed-through ports are positioned about 7 inches from the bottom. A gas port is located at the top. The feed-through ports consist of a glass extension fitted to a Kovar tube to which is brazed a brass collar or ring (Figure 2). Brass plugs fit into the Kovar tube and are sealed with "O" rings. The brass plugs have been drilled to hold metal rods that hold the internal hardware and are used for electrical feed-throughs (Figures 1, 3, and 4). The metal feed-through rods can be rigged for cooling with water while static (Figure 3) or rotating (Figure 4). The section of cathode feed-through rod inside the bell jar should be insulated with quartz because the cathode gets hot during sputtering.

The chromium cathode is fixed through port #1. It is a 1/4" thick X 4" diameter disc of steel or steel alloy with at least a 0.025" chromium plate. An aluminum shield is placed against the back of the cathode to keep it from sputtering.

The specimen holder may need to rotate so the brass plug in port #2 is rigged with a nylon bushing in addition to the proper "O" rings. The holder is rigged so that it can be cooled while rotating (Figure 4). An adapter is affixed to the end of the rod to hold either panels or rods.

The anode (and shield) at port #3 is an aluminum panel approximately 4" wide by 6" long bent to approximately a 3" radius. The anode is positioned between the chromium disc and titanium specimen. In this position using the shield as an anode, sputter cleaning of the chromium disc (cathode) or the titanium (cathode) may be obtained. Simultaneous cleaning of both titanium and chromium can also be done. The shield shape of the anode prevents the deposition of metal onto the cathode not being cleaned. After the titanium is cleaned, and the chromium cleaned and actively sputtering, the shield is rotated 180° to the far side of the titanium specimen. Now the chromium can deposit on the titanium specimen. The specimen holder may rotate to ensure complete cleaning and coverage.

PROCESS C - Sputter Operation

1. After chemical cleaning, the specimen is immediately mounted in the sputtering chamber.

2. Cleanliness of the vacuum chamber is extremely important. Care must be exercised so that no soil enters or develops within the vacuum sputtering system.

3. An extended period of pumping is now desirable to clear the system of all out-gassing. Poor pumping, contamination, or leaks in the system are flaws that may be noticed at this stage.

4. During this period, purging with high purity argon is usual to help clean the system.

5. A sputtering unit that is operating daily with the same hardware, will reach a level of efficiency and/or cleanliness that only a minimum cycle of pumping and purging (Item 3 and 4) may be needed. The minimum amount of pumping (Item 3) is one hour. The purge cycle is flushing 15 times with argon (pumping away the argon between flushes) then 15 minutes of high vacuum pumping and again 15 flushes of argon. A new system of hardware or a system used after a long shutdown without storage under vacuum, may require many hours of high vacuum pumping (Item 3) and even then the first runs may be unpredictable.

6. In a clean and efficient system, the cleaning of the specimen and the chromium cathode can be done simultaneously. The cleaning of the cathodes can be observed by the appearance of the metal, by deposition on the anode and by the color of the glow discharge. The color of the glow discharge will change from a red purple to a blue as

the cleaning progresses. On the rod specimen and chromium disc, 15 minutes of cleaning was sufficient once it was determined that the cleaning had started. A good run starts to show cleaning in about 10 minutes. As the titanium cleaning cycle progresses, the titanium heats up. If the vacuum system leaks or is contaminated from some internal source, the titanium may gradually get dirty instead of becoming clean.

7. When the titanium is sufficiently clean and the chromium is sputtering, rotate the shield 180° so that the titanium specimen is between the shield (anode) and the chromium disc (cathode) . Immediately disconnect the titanium so that it is no longer cathodic. Chromium will begin to deposit upon the titanium specimen. Some influences on the rate of deposition are the distance of the specimen from the cathode, masking of the specimen (its own shape -- it may need to be rotating), and the voltage/current setting. The length of sputtering (and/or cleaning) time is limited due to the heating of the cathode unless adequate cooling is provided. For the purposes of this study, thicknesses obtained in up to one hour of sputtering were adequate. At the end of the sputter run, the bell jar is kept closed for about an hour so that the hardware can cool under vacuum or inert gas.

PROCESS D - Electroplating

The titanium specimen is removed from the bell jar using clean gloves and handled carefully so that the specimen is not soiled. The specimen is quickly masked if it is required then placed directly into a plating bath. Conventional plating methods and ⟶

SECTION III - PROCESS D CONTINUED

solutions should be acceptable except that the specimen is immersed into the plating bath with a pre-set plating voltage to ensure no standing in solution or reverse etching.

PROCESS E - Additional Information

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Section III has been written so that it can be extracted and used as a process or production procedure. The procedure is described generally, because each specific specimen would have to be handled slightly different due to its shape, required masking, or other considerations.

Masking

The specimen can be masked in the sputtering chamber by shielding it from metal deposition with aluminum foil. Make sure that the masking will not entrap gasses that will slowly escape and cause difficulty.

Voltage Setting

A minimum voltage for "breakdown" is required in order to obtain a glow discharge. Increasing voltage at a fixed partial pressure of gas, will increase the current. This increased wattage will increase the sputter rate, however, arc discharging may occur at the higher voltages. Too high a power setting will liberate more heat which can become a problem on vacuum seals, excessive out-gassing and heating of the cathode surface to its melting point.

SECTION III - PROCESS E CONTINUED

In the glow discharge, generally near the surface of the cathode, is a dark zone. This zone is called the dark-space. The distance between the dark-space and cathode surface varies with voltage. The distance from this dark-space to the specimen, is more important than the distance from cathode to specimen. This is important becuase the sputter deposition rate and uniformity of thickness drops off as the distance increases.

PROCESS F - Specific Details

Section III, A to F, describes generally this procedure for placing chromium over titanium and is usuable as a production procedure. Specific details applicable to the 1" X 3" panels and 1/8" diameter X 4" rods described in this paper, are given below.

Chemical Cleaning Procedure

The rods and panels were handled as described in this section, except that only 10 to 15 ml of acid cleaning solution was used and only until the titanium became bright.

Sputter Cleaning of the Titanium

For the cleaning of titanium, a minimum of 2000 volts is required to "break through" and initiate the sputtering. The current is fixed so that a power density of about 0.7 watts/cm is obtained. On a 1" X 3" panel (set for both sides) a setting of 2000 volts and 15 milliamperes was used. The 1/8" diameter X 4" rods, were cleaned simultaneously with the chromium cathode with 2000 volts and 20 milliamperes. —>

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SECTION III - PROCESS F CONTINUED

Sputter Deposition of Chromium

The sputtering rate range on 1" X 3" panels and 1/8" diameter rods is from .5 microns to 1.5 microns per hour at a distance of approximately 3" and a setting of 2000 volts and 60 milliamperes. The partial pressure of Argon in the chamber during the sputter cleaning and sputter deposition is in the range of 10 to 50 microns.

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Electroplating

The bath generally used on the 1/8" rods, was a 400 gm/l CrO_3, 10 gm/l SO_4 at 55°C. Except as noted, the power was supplied by a 115 volt single phase rectifier filtered with a 6 volts storage battery connected across the output. The plating was done in a 1 liter beaker placed in a temperature controlled water bath. A circular lead-antimony anode was used. A current density of 3.5 ASI gave a build up of approximately 1 mil/hr.

SECTION IV - TEST RESULTS

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Sputter Cleaning

Unless otherwise noted, all titanium specimens described in this report, were sputter cleaned simultaneously with the chromium cathode. Voltage was fixed at 2000 volts and the current at 20 milliamperes. Sputtering usually started within 10 minutes, afterwhich 15 minutes of actual sputter cleaning was found to be sufficient.

Sputter cleaning tests were run on 1" X 3" titanium panels. Uniform stock removal was assumed.

Initial sputter cleaning runs were made only on the 1" X 3" titanium panel and not simultaneously with the chromium cathode. Three power levels were used that included 5 different voltage/current combinations. They gave removal rates of from 0.8 microns to 2.2 microns/hr. Voltages tried varied from 1500 volts to 2500 volts and the current settings varied from 15 milliamperes to 40 milliamperes. Figure 5 shows the effect of current on titanium removal (1 " X 3" panel) for a fixed voltage and a fixed time.

Additional 1" X 3" titanium panel samples were cleaned while simultaneously cleaning the chromium. The titanium and chromium are both cathodes and because of the shunting effect to the chromium, the amount of titanium removed is much less. Figure 6 shows the effect of varying current at a fixed voltage and time while simultaneously cleaning the chromium cathode and the titanium panel.

A 15 minute sample was included in Figures 5 and 6. They indicate linearity of removal with time.

Chromium Sputtering

Sputter deposition on all specimens, including those for spin testing, was done at 2000 volts and 60 milliamperes. Because the voltage/current setting is reasonably fast and gives good control, it was made standard for all specimens.

Chromium deposition rates were obtained using the 1" X 3" titanium panels. A weight was obtained on the titanium panel before and after chromium deposition and thickness estimations were based on the increase in the weight. The titanium panels were therefore not sputter cleaned during the cycle. The 4" diameter chromium disc was used for the cathode. Distance from the cathode to the specimen was approximately 4 inches. Deposition rates were calculated at 2 power settings and a total of eight different voltage-current settings. The deposition rates by thickness varied from approximately 0.12 microns/hr at 1500 volts - 45 ma, to approximately 0.55 microns at 3000 volts/80 ma. Figure 7 shows the influence of some conditions on the deposition rate on panels.

Deposition will not only vary with the parameters already mentioned, but the shape of the specimen will also influence the deposition rate. Cross-section photomicrographs on 1/8" titanium rods indicate a build up approximately three times as thick as a panel for the same conditions. Compare 2000 volts, 60 ma, 60 minutes, points in Figures 7 and 8. (To verify the validity of converting weight increase to thickness, a panel checked both ways gave agreement to within 10%.)

SECTION IV - TEST RESULTS CONTINUED

Typical build up of chromium by sputtering on 1/8" (approximately) titanium rods, is shown in Figure 8. The thickness readings were obtained from photomicrographs and are subject to wide variations. Photographs were made at 1000 X and specimens held at 10° to gain another 6X in width of the sputtered layer. Total magnification was therefore, approximately 6000 X in one direction and the data appears to be quite reasonable.

Effect of Sputter Rate on the Sputtered Chromium

No apparent difference in hardness or grain structure was detected in the sputtered chromium layer due to rate of deposition. A comparison was made between two specimen panels one of which was sputtered at 2000 volts and 60 ma, for 10 hours and other sputtered at 2000 volts and 30 ma for 20 hours. Long sputter times were required in order that a depth of sputter chromium would be obtained suitable for measurements. The specimens were chromium plated and mounted at an angle so that microhardness measurements could be made. Care was exercised that the indentation stayed within the sputtered layer. The results are shown in the first and second columns of Table 1.

The angle of the mount placed the titanium under the sputtered chromium when the microhardness was made. Readings on the titanium are included for comparison.

(The readings indicate that the chromium is in a well annealed state) No grain structure was apparent in either sample, nor was any observed in any subsequent samples.

Effect of Hydrogen During Sputtering

No apparent difference was noted on the hardness or grain structure of the sputtered chromium layer due to incorporation of 0.1% hydrogen into the argon atmosphere during sputtering. A panel was prepared by sputtering for 10 hours at 2000 volts and 60 ma in an atmosphere (partial pressure) that contained 0.1% hydrogen in argon rather than pure argon that is normally used. Other than for the incorporation of the hydrogen during sputtering, the sample was prepared exactly like the normal desposition sample in the previous paragraph (Table 1, column 2). Hardness data on this sample is shown in Table 1, column 3. It is apparent that the amount of hydrogen used, did not effect the hardness. No grain structure was apparent.

Preliminary Spin Tested Samples

The first group of titanium rods that were spin tested, showed a fair degree of adhesion. The rods were tested by William H. Dancy, Jr., head of the Instrumentation Development Group, Research Laboratories for the Engineering Sciences, University of Virginia, Charlottesville, Virginia, using the procedure outlined in his Report No. EP 4424-105-61U.

TABLE I

HARDNESS OF CHROMIUM VS DEPOSITION RATE AND ATMOSPHERE

Atmosphere:	Pure Argon	Pure Argon	0.1% H_2 in Argon
Deposition Rate:	Slow Deposition	Normal Deposition	Normal Deposition
VHN - 1 gm	Cr 290 Ti 190	Cr 270 Ti 175	Cr 300 Ti ---
VHN - 15 gm	Cr 265 Ti 185	Cr 270 Ti 190	Cr 270 Ti 190

All of the rods in this group were treated as outlined and electroplated with the apparatus as described in Section III, except that an unfiltered power supply was erroneously used. The chromium appearance was frosty or gray, rather than bright because of the unfiltered power supply. The electroplating bath used in this group was 400 gm/l CrO_3, 10 gm/l SO_4, operated at 65°C. The individual rods differed as follows:

Rod # 1 - - alpha beta titanium (2 iron, 2 chromium, 2 molybdenum) Sputter cleaned for 15 minutes (simultaneously with the chromium cathode) at 2000 volts and 20 milliamperes. Voltage pre-set for electroplating so that direct plating results without any reverse etch or chemical etch. Electroplated at 2 ASI, for 2 hours, then stopped and examined. Placed back in plating bath, reverse etched for 30 seconds at 1 ASI, plated again for 18 hours.

Rod # 5 - - treated the same as Rod #1 (interrupted electroplate) except that the rod is alpha titanium.

Rod # 6 - - material is alpha titanium treated like the previous rod, except that the electroplating was not interrupted but was continuous for 20 hours.

Rod # 7 - - 4140 steel control rod, cleaned 2 minutes cathodically and 1/2 minute anodically in hot alkaline solution at 1 ASI. No sputtered chromium. Electroplate started with a reverse etch at 1 ASI for 30 seconds. Plating interrupted then continued as in rods 1 and 5.

Rod # 8 - - steel rod like #7, except plating was continuous once started as with Rod # 6.

SECTION IV - TEST RESULTS CONTINUED

The spin test results are summarized in Table II. This series of tests implies that with a proper cycle (continuous plate - Rod #6) adhesion to titanium can be as good as adhesion to steel (Rod #8). However, it must be noted that the adhesion of chromium to steel rods falls far short of the strength (approximately 50,000 PSI) that it should exhibit. The only probable cause was thought to be the use of the unfiltered plating power supply. The second group of rods that were spin tested were plated with a filtered power supply. The surface appearance of the chromium was bright and the value of the bond on steel was normally high.

It was however, of interest to note the location of failure. It was apparent that the electroplated chromium was removed. It appeared that sputtered chromium still remained and that the failure was either at the plating interface of the sputtered chromium, or near the interface. This was determined by plating three tested rotors from Rods, 1, 5 and 6. Each plated without any pre-treatment indicating that the surface was probably still chromium rather than titanium. These rotors were then mounted as described in Section IV - Sputter Cleaning and photomicrographs of these and untested portions of the same rod were compared. Substantially the same amount of sputtered chromium was present in both the tested and untested portions.

Effect of Sputter Thickness and Other Variations On Adhesion of Chromium Plate

Results obtained from the second and third groups of spin tested rods show no apparent correlation between the thickness of the sputtered chromium and the strength of the chrome-plated bond.

TABLE II

ADHESION TEST DATA

Chromium Plate Rods Tested By W.H. Dancy
Electroplated With Unfiltered Power Source

Rod No.	Sample No.	Test No.	Substrate Diameter Inches	Plate Thickness Inches	Maximum Speed on Failure RPS	Maximum Stress on Interface PSI	Remarks
7	2	12:9:66B	0.1223	0.0121	15,500	5,360	Small chips thrown off
Steel Control	3	12:9:66A		0.0116	8,350	1,470	20% of bond failed
Interrupted	3	12:13:66B		0.0116	18,900	6,790	100% of bond failed
Electroplate	4	12:9:66C		0.0107	17,150	5,680	100% of bond failed
	6	12:13:66C		0.0106	11,550	2,550	Small chips thrown off
	6	12:14:66A		0.0106	13,625	3,550	Small chips thrown off
8	1	12:12:66A	0.1223	0.0112	14,800	4,460	80% of bond failed
Steel Control	2	12:13:66A		0.0107	24,625	11,720	100% of bond failed
Continuous Electroplate	3	12:13:66D		0.0103	22,070	9,010	Rotor lost in vacuum System
1	1	1:5:67D	0.1221	0.0116	13,170	3,660	Small chips thrown off
Alpha-Beta Ti	1	1:6:67A		0.0116	17,020	6,110	90% of bond failed
Interrupted	2	1:6:67B		0.0113	20,340	8,510	80% of bond failed
Electroplate	3	1:6:67C		0.0123	19,350	8,460	100% of bond failed
5	1	1:4:67A	0.1087	0.0129	16,500	5,930	Small chips thrown off
Alpha Ti	1	1:4:67B		0.0129		5,580	50% of bond failed
Interrupted	2	1:5:67A		0.0122	20,100	8,290	100% of bond failed
Electroplate	3	1:5:67B		0.0118	14,320	4,020	Small chips thrown off
	3	1:5:67C		0.0118	18,400	6,630	70% of bond failed
6 Alpha Ti	1	1:9:67A	0.1220	0.0114	23,350	11,320	Rotor lost in Vacuum System
Continuous	2	1:9:67B		0.0110	25,200	12,580	100% of bond failed
Electroplate	3	1:9:67C		0.0106	24,400	11,360	90% of bond failed

The second and third groups were plated differently than the earlier group. The bath temperature was dropped to 55°C and the current density increased to 3.5 ASI. More important because it resulted in a bright chromium finish, was the inclusion of a six volt battery in parallel with the plating rectifier to filter the current. All rods were alpha-beta titanium and electroplated for 20 hours. Electroplating of the rods was started immediately because a voltage was pre-set and no chemical etch due to standing or reverse etch used except where noted. The rods checked in the second group were made as follows. The adhesion data is shown in Table III and Table IV.

Rod #11 -- 60 minute sputter, normal sputter, normal conditions, like rod #6 from the first group, except rod #6 was plated with an unfiltered power supply, whereas this rod was plated with a filtered power supply.

Rod #12 -- Same as # 11, except this rod has a 30 minute sputter.

Rod #13 -- Same as #11 except this rod has a 15 minute sputter.

Rod #14 -- Steel control rod, same as Rod #8, except this was electroplated with a filtered rectifier.

Rod #15 -- Same as #11, except that the first 15 minutes of the electroplating was with the rectifier not filtered.

Rod # 16 -- Same as #11, except that the electroplating was preceded with a 15 second reverse etch at 1 ASI. (A typical plating procedure to initiate chromium plating over a chromium substrate.)

Rod # 17 -- Same as Rod # 11, except sputtering was for 10 minutes.

Rod # 18 -- Same as Rod # 11, except sputtering was for 5 minutes.

The third group of spin tested rods were prepared as described below and the adhesion values are shown in Table IV.

Rod # 20 -- Same as # 15, except the first 30 minutes is with an unfiltered power supply.

Rod # 21 -- Same as # 15, except the first 7 1/2 minutes is with an unfiltered power supply.

Rod # 23 -- 20 minutes of sputtering, with the first 15 minutes of electroplating with an unfiltered power supply.

Rod # 25 -- Sputtered for 5 minutes, placed in the plating bath without a pre-set voltage. Rod, therefore, may have been bath etched a few seconds before plating was initiated.

The second group of spin tested rods appeared to develop a relationship between the sputtered thickness and adhesion and also an improvement in adhesion if the initial plating was done with an unfiltered plating supply. The third group does not support either conclusion. Too few samples were made to draw any firm conclusions. In general, it appears that a tensile strength of 10,000 to 15,000 PSI can be obtained with 15 to 60 minutes of sputtering.

According to W. H. Dancy, the level of adhesion demonstrated by the optimum samples in this process is substantially higher than any other chromium plate over titanium system that he has checked by spin testing.

TABLE III
ADHESION TEST DATA
Chromium Plated Rods Tested By W.H.Dancy
Electroplated With a Filtered Power Source

Rod No.	Sample No.	Test No.	Substrate Diameter Inches	Plate Thickness Inches	Maximum Speed at Failure RPS	Maximum Stress on Interface PSI	Remarks
11	1	4:17:67B	0.1085	0.0263	12,650	8,730	50% of coating failed
Alpha Ti	2	4:18:67B		0.0263	12,350	8,320	50% of coating failed
60 Minute Sputter	3	4:18:67C		0.0257	12,800	8,660	90% of coating failed
12	1	4:17:67A	0.1155	0.0179	17,750	10,750	100% of coating faile
Alpha Ti	2	4:17:67D		0.0181	20,900	15,170	100% of coating faile
30 Minute Sputter	3	4:18:67A		0.0182	18,150	11,520	100% of coating faile
13	1	4:17:67C	0.1166	0.0147	17,900	8,680	70% of coating failed
Alpha Ti	2	4:18:67E		0.0152	21,870	13,450	100% of coating faile
15 Minute Sputter	3	4:18:67D		0.0157	23,750	16,510	100% of coating faile
14	1	4:24:67E	0.1250	0.0200	34,220	48,940	100% of coating faile
Steel Control	2	4:25:67A		0.0194	35,300	50,240	100% of coating faile
	3	4:25:67B		0.0190	34,530	46,660	100% of coating faile
15	1	4:19:67C	0.1143	0.0237	18,070	16,020	100% of coating faile
Alpha Ti	2	4:24:67B		0.0234	17,500	14,800	100% of coating faile
60 Min. Sputter First 15 Min. Plating Unfiltered	3	4:24:67D		0.0228	14,470	9,780	100% of coating faile
16	1	4:19:67A	0.1070	0.0199	Coating Failed at Less than 6000 RPS		
Alpha Ti.	2	4:19:67B		0.0192	5,900	1,240	75% of coating failed
60 Min. Sputter	3	4:19:67D		0.0191	5,920	1,240	15% of coating faile
15 sec. Reverse	4	4:24:67A		0.0182	9,500	Small Chip Pulled From Coating	
Etch before Plating	4	4:24:67C		0.0182	13,200	5,810	100% of coating faile

TABLE IV

ADHESION TEST DATA

Chromium Plated Rods Tested by W.H. Dancy

Rod No. (All Rods Alpha Ti)	Sample No.	Test No.	Substrate Diameter Inches	Plate Thickness Inches	Maximum Speed at Failure RPS	Maximum Stress on Interface PSI	Remarks
17	1	4:25:67C	0.1060	0.0185	16,670	9,370	60% of coating failed
10 Min. Sputter	2	4:25:67D		0.0182	20,000	13,110	100% of coating failed
Filtered Electro-	3	4:26:67A		0.0180	11,700	4,440	Sample lost in vacuum system
plate	4	4:26:67E		0.0175	17,760	9,870	100% of coating failed
18	1	4:26:67B	0.1090	0.0188	16,070	9,070	100% of coating failed
5 Min. Sputter	2	4:26:67C		0.0190	12,900	5,920	100% of coating failed
Filtered	3	4:26:67D		0.0190	14,340	7,300	100% of coating failed
Electroplate							
20	1	5:23:67B	0.1120	0.0137	22,100	11,670	Small chip pulled off
60 min. Sputter	1	5:24:67B		0.0137	24,990	14,920	Most of chromium pulled off
First 30 min.	2	5:23:67A		0.0138	20,300	9,930	50% of chromium pulled off
Plate Unfiltered	3	5:23:67C		0.0139	25,750	16,200	Most of chromium pulled of
21	1	5:22:67D	0.1077	0.0272	16,050	14,670	Most of chromium pulled off
60 Min. Sputter	2	5:22:67A		0.0267	14,550	11,740	Small chip pulled off
First 7 1/2 Min.	2	5:22:67B		0.0267	13,950	10,790	Most of chromium pulled off
Plate Unfiltered	3	5:22:67C		0.0262	15,450	12,040	Most of chromium pulled off
23	1	5:22:67G	0.1175	0.0197	8,200	2,630	50% of chromium pulled off
20 Min. Sputter	2	5:22:67F		0.0198	10,620	4,450	25% of chromium pulled off
First 15 Min.	3	5:22:67E		0.0199	15,870	10,030	Most of chromium pulled off
Plate Unfiltered							
25	2	5:23:67D	0.1167	0.0182	15,050	7,690	Small chip pulled off
5 Min. Sputter	2	5:24:67A		0.0182	17,650	10,940	Most of chromium pulled off
Bath Immersed	3	5:23:67E		0.0182	18,810	12,430	Most of chromium pulled off
Prior to Plate							

Hardware Samples

The process was used successfully on some commercially pure titanium bolts, demonstrating a practical use. The bolts used were 1/4" X 20" X 3" hex head. The threads on these bolts were quite sloppy so it was difficult to demonstrate control of tolerances by controlling chemical etch and plating thickness. Nevertheless, chemical cleaning was kept minimal and the bolt was sputter cleaned and deposited. The geometry and size of the bolt was not too unlike the rods, so that no changes were made in the parameters. The bolt was electroplated for 2 hours with the improved bath described in Section IV, Effect of Sputter Thickness and Other Variations on Adhesion of Chromium Plate. The appearance of the bolt is comparable to that of our best rod samples.

High Temperature Effect on Sample

The use of a chromium electroplate may be a convenient way of providing a high temperature protective coating on titanium. One section of a titanium rod was electroplated with chromium to a depth of 4 mils. The other part of the titanium (alpha-beta) rod was not protected. The entire rod was placed in a furnace, open to atmosphere and held at 1500°F for 22 hours. The bare titanium suffered from scaling and oxidation, lost approximately 1 mil of surface and presented a poor surface appearance. The chromium plated surface was green with oxide, but when brushed away still presented a relatively good surface. It had lost only about 1/2 mil of surface. A photomicrograph of the cross-section shows formation of a wide band (approximately 2 mils) of what is apparently a new alloy.

SECTION V - CONCLUSIONS

1. An adherent chromium electroplate was obtained on titanium through the use of a sputtered intermediate layer of chromium. Values up to 16,000 PSI were obtained in spin testing.

2. The crux of the procedure is placing the sputtered intermediate layer over the titanium immediately after rendering the titanium ultra-clean by sputter cleaning.

3. A minimum voltage is required in order to initiate sputtering. Increasing the wattage will increase the sputter rate, however, the surface temperature of the metal being sputtered (cathode) will also increase. The hot cathode (especially titanium, when it is being cleaned) becomes more reactive with any contaminants that may be present in the sputtering system. It is apparent that a faster rate can therefore be utilized in a cleaner system and if the cathode can be cooled.

4. Good adhesion of electroplated chromium was obtained on as little as 0.2 micron thickness of sputtered chromium intermediate.

5. No effect was apparent on the structure or hardness of the intermediate layer due to the rate of deposition nor to the inclusion of 0.1% hydrogen in the argon gas used in the sputtering system.

6. Poorer adhesion results were obtained if at the start of the electroplating (1) a reverse etch was employed, (2) if a pre-set voltage was not used (in order to assure immediate plating rather than a momentary chemical etch), (3) if an unfiltered power supply was used.

END

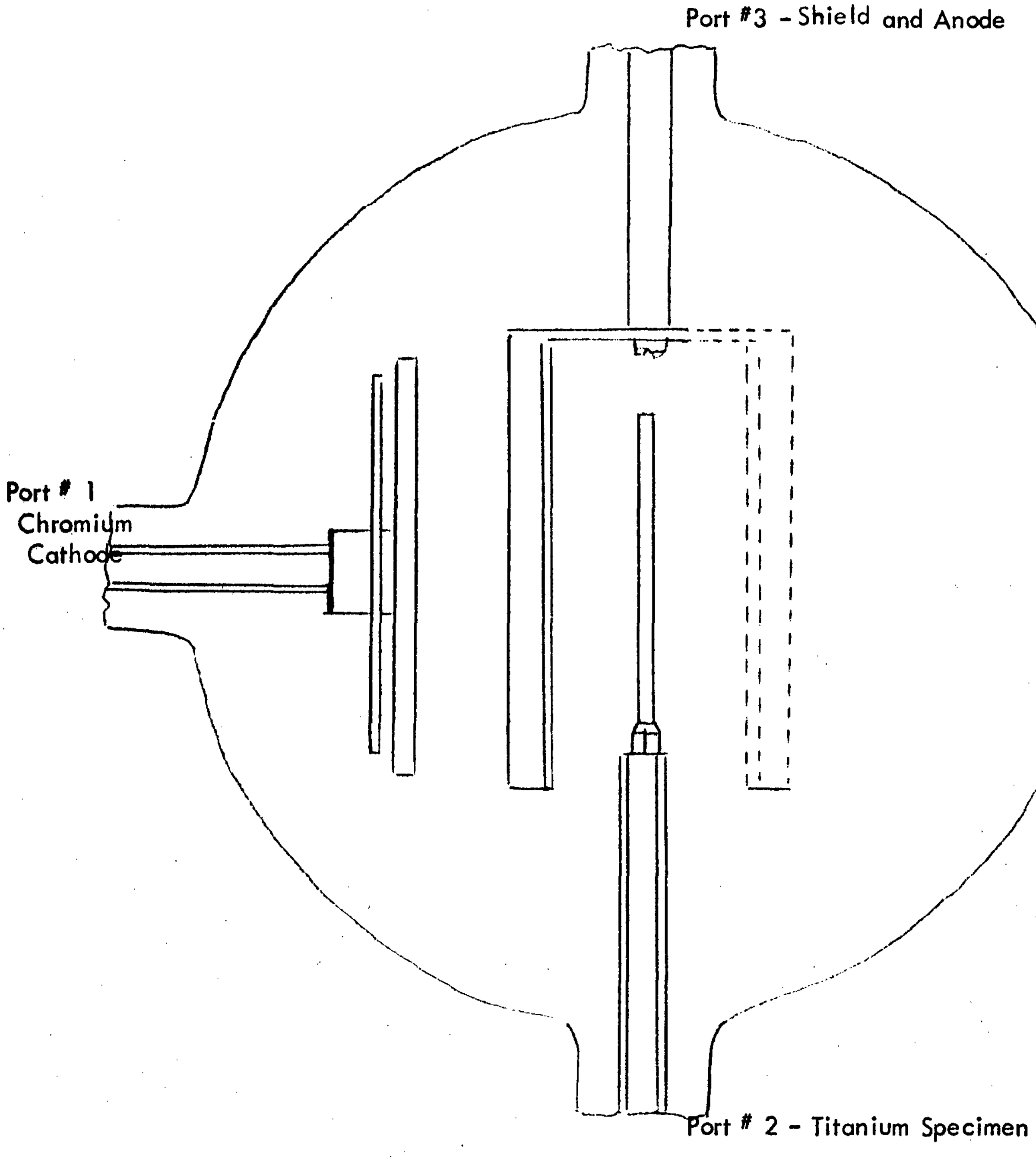


FIGURE 1

BELL JAR - TOP VIEW

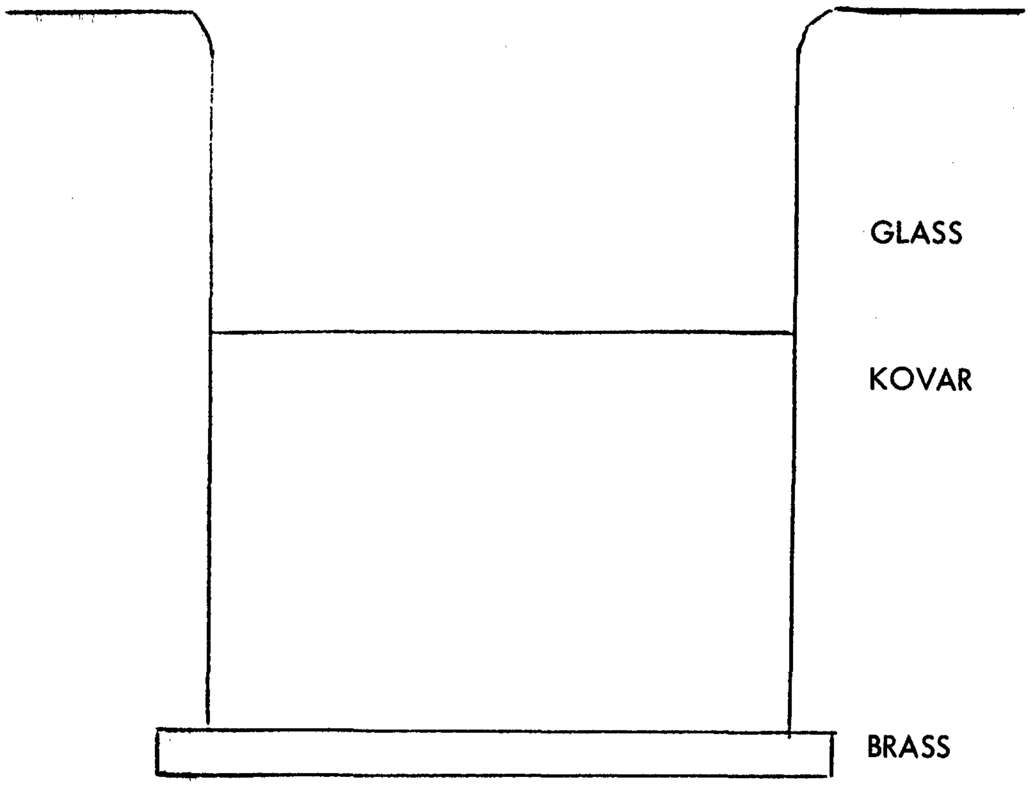


FIGURE 2

FEED - THROUGH PORT

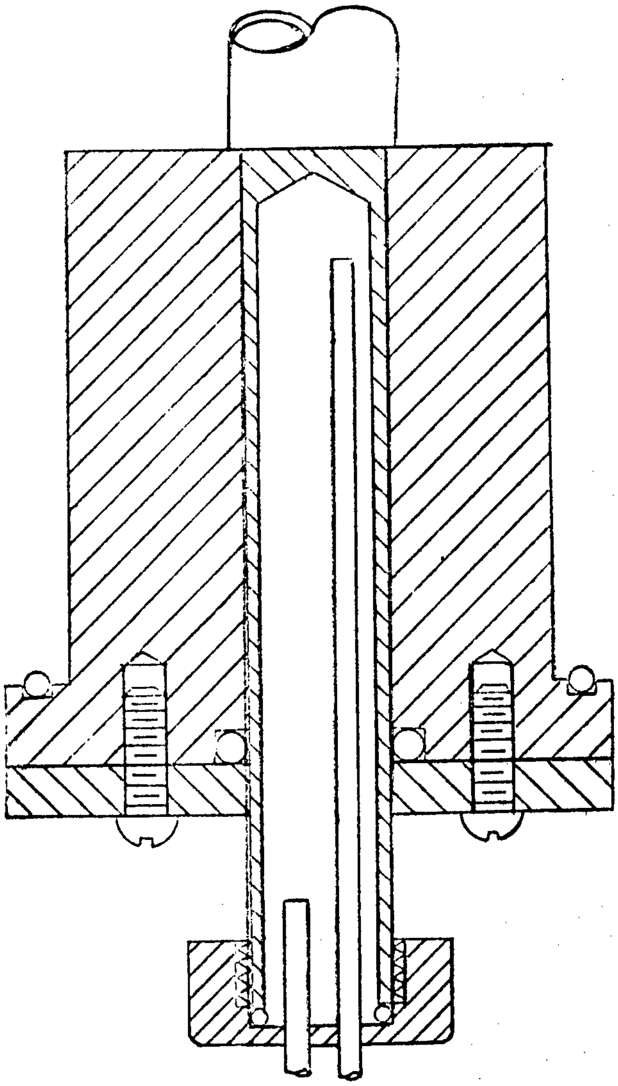


FIGURE 3

BRASS PLUG
Showing Static Feed-Through Rod, "O" Rings and Cooling

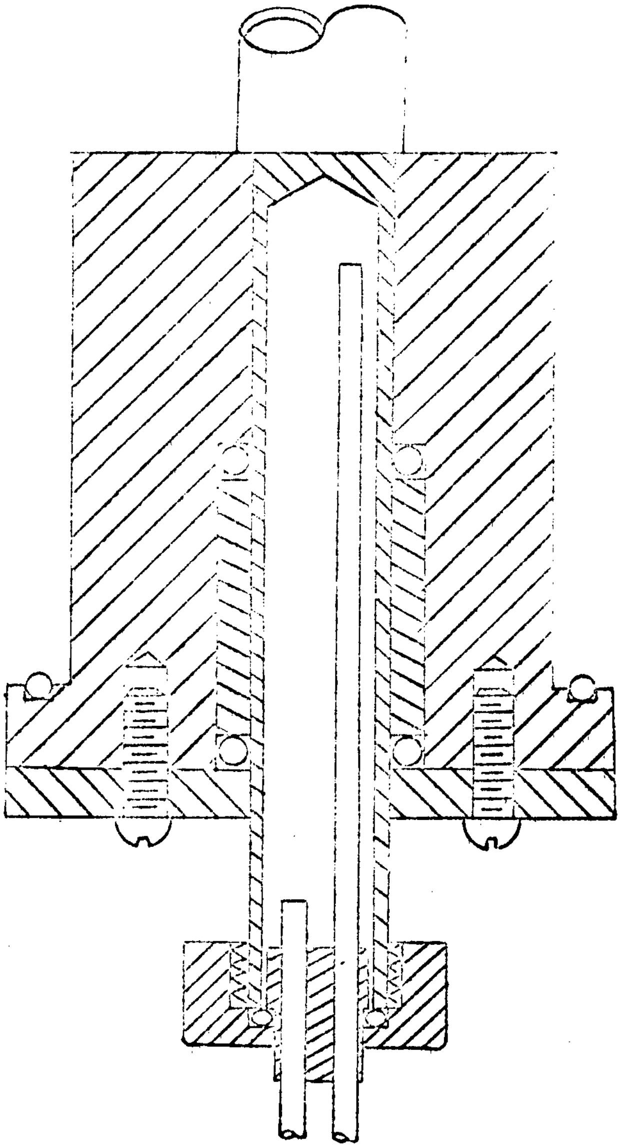


FIGURE 4

BRASS PLUG
Showing Dynamic Feed-Through Rod, Nylon Seal, "O" Rings and Cooling

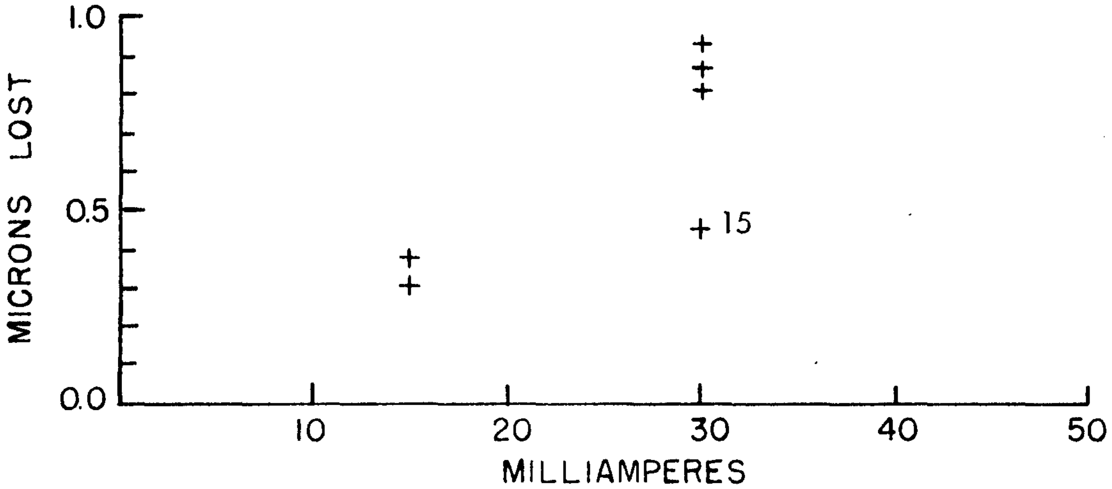


FIGURE 5

SPUTTER CLEANING

1" X 3" Titanium Panel at 2000 Volts For 30',Except as Shown,Thickness (Microns) Converted From Weight

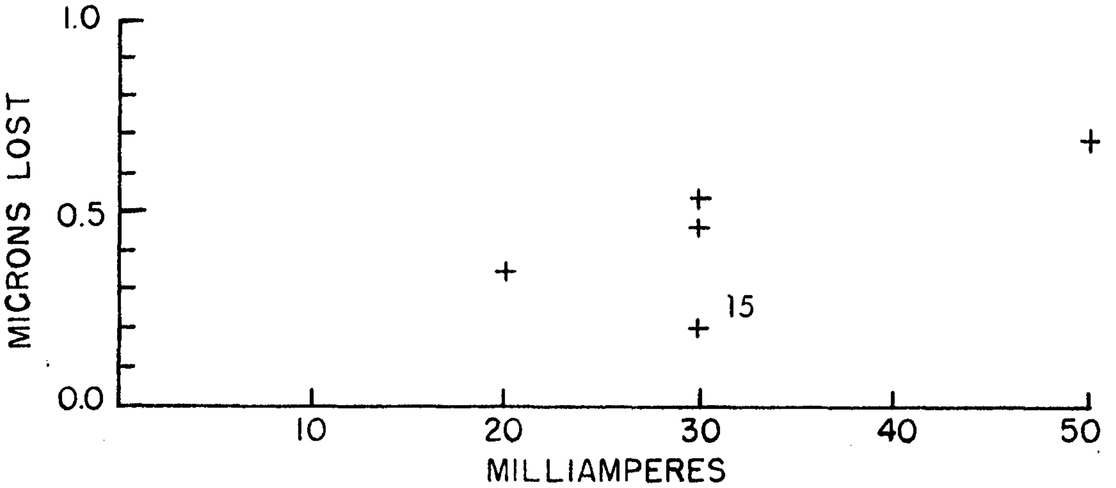


FIGURE 6

SPUTTER CLEANING

1" X 3" Titanium Panel - Simultaneously With Chromium Cathode at 2000 Volts For 30',Except As Shown,Thickness (Microns) Converted From Weight.

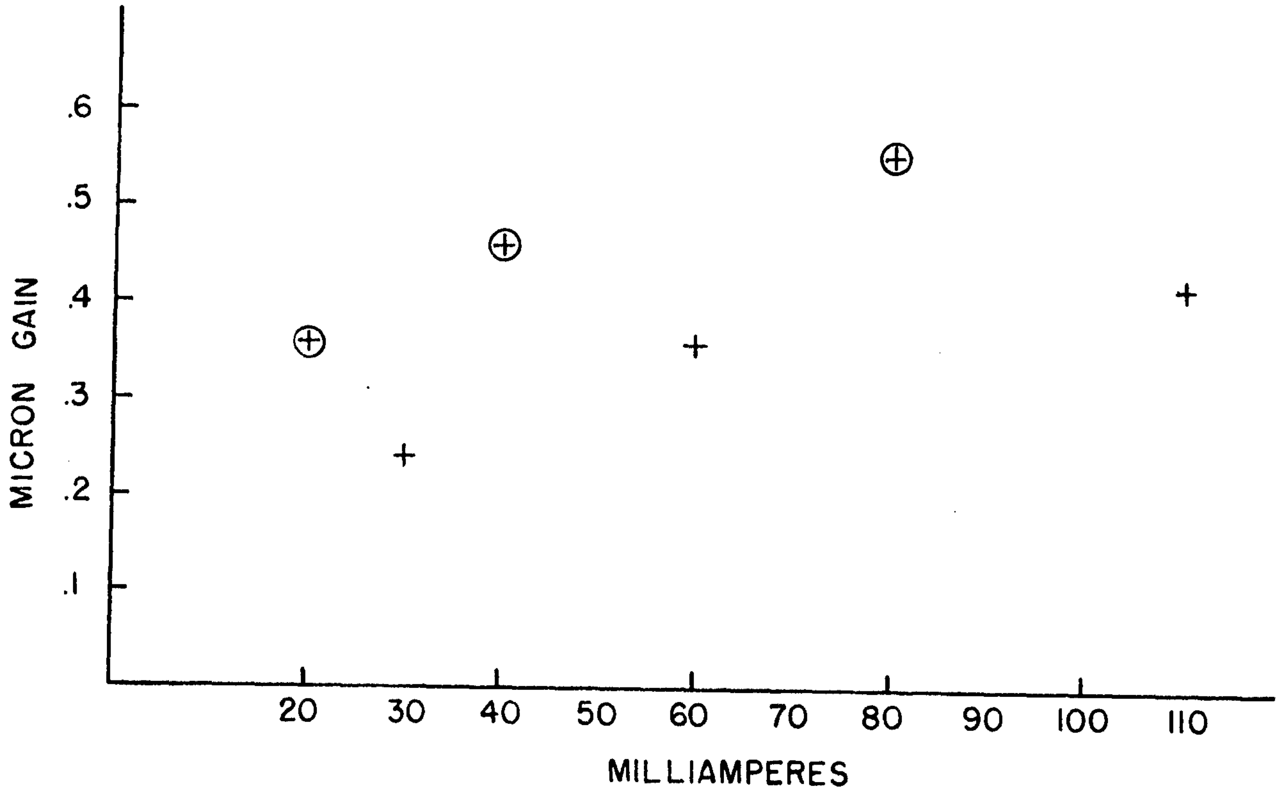


FIGURE 7
CHROMIUM DEPOSITION ON 1" X 3"
Ti PANELS

+ 2000 Volts
⊕ 3000 Volts

Weight Gain is Converted Into
Thickness Gain - Sputtered For
60 Minutes

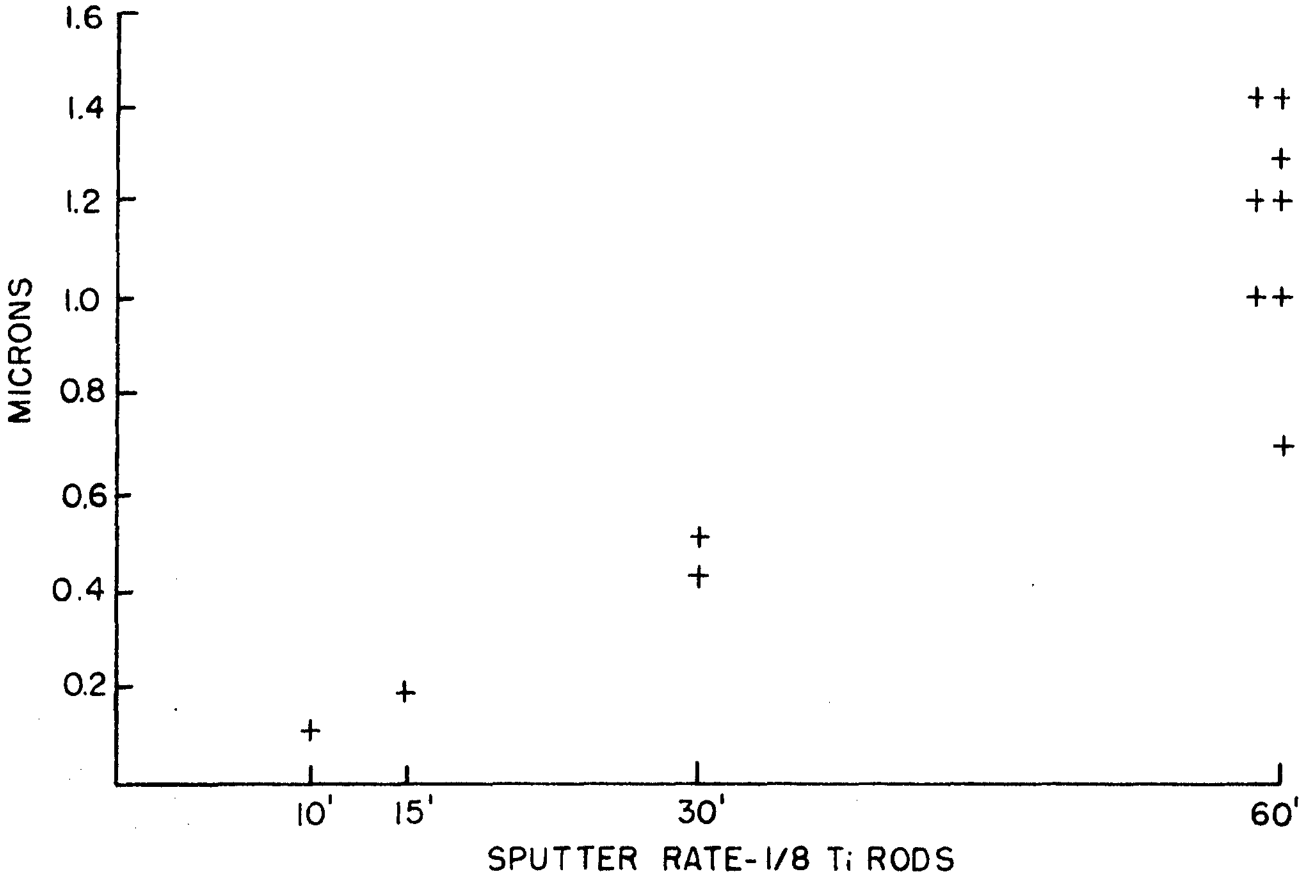
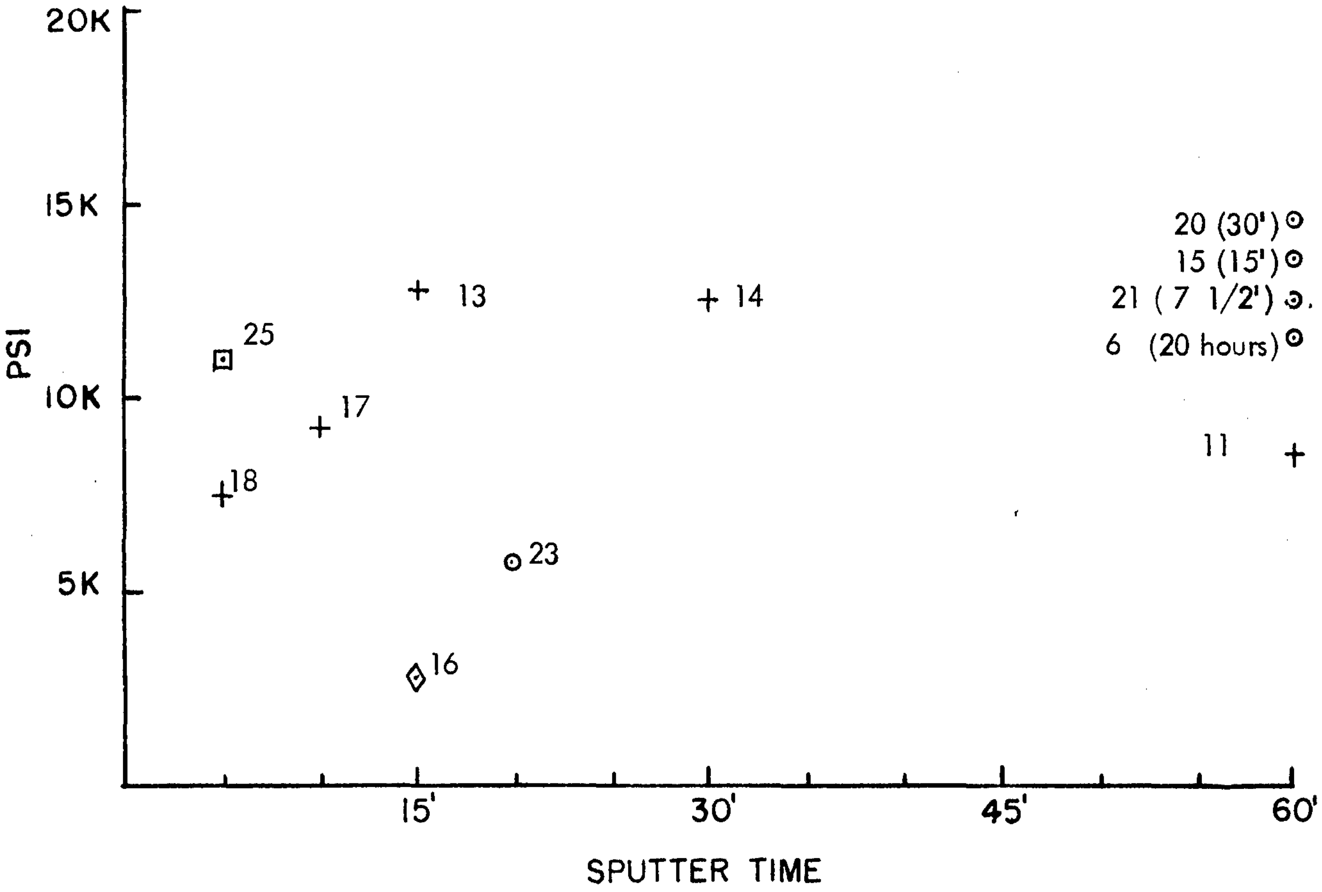


FIGURE 8

2000V/60MA, THICKNESS IN MICRONS BY PHOTOMICROGRAPH, SPUTTER RATE ON RODS



- \+ Pre-set Voltage - Filtered Supply
- ⊙ No Filter (Time as Shown) - Then Filtered Supply
- ⊡ No Voltage Set
- ◊ Reverse Etch (1 ASI - 15 Sec.)

NOTE: Rod Numbers are Shown

FIGURE 9
TENSILE STRENGTH VS SPUTTER
TIME AND PLATING VARIATION

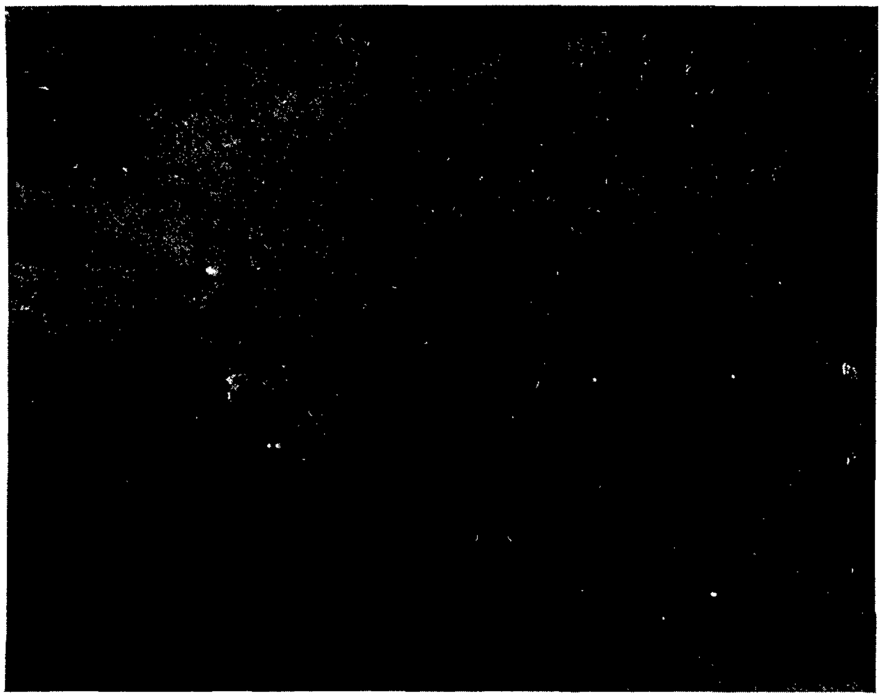


FIGURE 10
Photo micrograph -- cross section of a titanium rod showing the sputtered chromium layer between the titanium and chromium electroplate

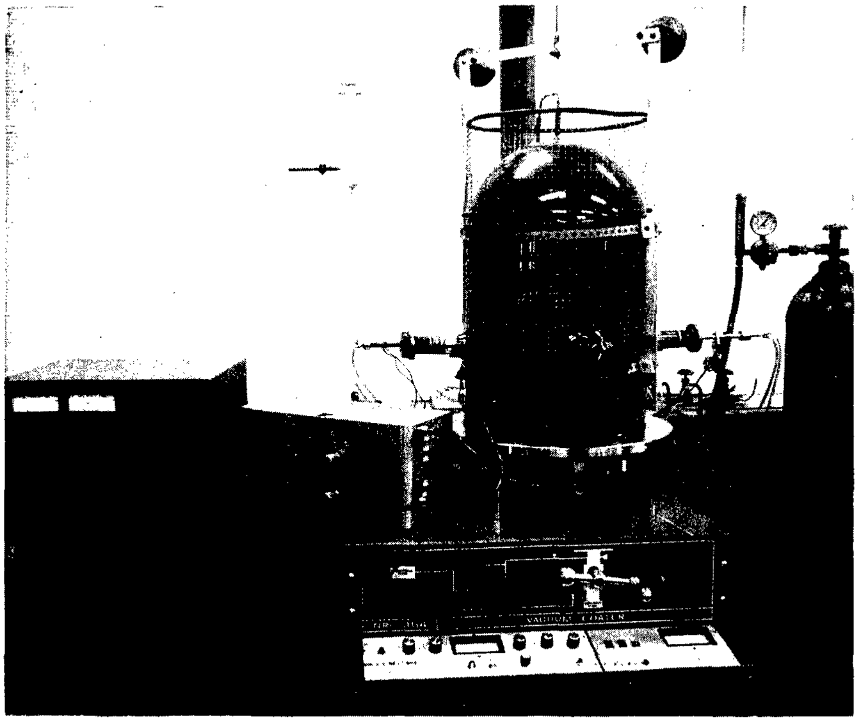


FIGURE 11
Bell Jar adapted for hardware -- power supply and gas control box are shown

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