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PREPARATION OF THICK MOLYBDENUM TARGETS

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Technique of preparation of thick molybdenum-100 targets on a copper substrate, for use in the production of Tc^{99m} isotope used in cancer therapy.

16. Abstract

Thick natural molybdenum deposits on nickel-plated copper substrates have been prepared by thermal decomposition of molybdenum hexacarbonyl vapors on a heated surface in an inert gas atmosphere. The molybdenum metal atoms are firmly bonded to the substrate atoms, thus providing an excellent thermal contact across the junction. Molybdenum targets thus prepared should be useful for internal bombardment in a cyclotron where thermal energy inputs can exceed 10 kW.

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PREPARATION OF THICK MOLYBDENUM TARGETS

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ABSTRACT

Thick natural molybdenum deposits on nickel-plated copper substrates have been prepared by thermal decomposition of molybdenum hexacarbonyl vapors on a heated surface in an inert gas atmosphere. The molybdenum metal atoms are firmly bonded to the substrate atoms, thus providing an excellent thermal contact across the junction. Molybdenum targets thus prepared should be useful for internal bombardment in a cyclotron where thermal energy inputs can exceed 10 kW.

INTRODUCTION

Molybdenum metal is used widely in such diverse industries as aerospace, steel, electronic, and agriculture. For example, molybdenum contributes to the hardenability and toughness of quenched and tempered steels. It is used in certain nickel-based alloys in order to increase their resistance to heat and corrosion in chemical solutions. It finds many uses in nuclear energy applications and in the manufacture of missile and aircraft parts. Molybdenum is also an essential trace element in plant nutrition. Even though there have been many technical advances in the production and fabrication of molybdenum, there are many applications where vapor-phase deposit can serve as an effective technical substitute for the solid metal. Furthermore, the composite parts so prepared are often superior to

either metal alone. It is therefore highly advantageous to develop techniques for vapor phase deposition of high temperature metals like molybdenum, tungsten, and tantalum.

Recently, Technology Utilization Office at Langley Research Center identified a need for efficient molybdenum-100 deposition on a nickel plated copper substrate. (See Appendix 1 for the problem statement.) This molybdenum-coated copper target would be used to produce Mo^{99} radionuclide via Mo^{100} (p, pn) Mo^{99} reaction at 27 MeV in a cyclotron. The decay scheme showing the basis of (Mo^{99} - Tc^{99m}) as a radiotherapeutic source is shown in Appendix 2 (ref. 1). The $(molybdenum)^{100}$ coated target would have to be exposed to an internal beam of the order of one-half milliampere at the above-mentioned voltage in order to produce sufficient amount of Mo^{99} radionuclide. The incident proton beam would lose about 13 kW of energy in the target, necessitating very efficient thermal cooling to prevent melting. In order to keep the molybdenum deposit temperature low during its bombardment, it is essential that the molybdenum deposit on the copper substrate be firmly adherent. The molybdenum coat thickness would also have to be a significant fraction of the distance traveled by the incident proton beam before its energy fell to the threshold value for Mo^{100} (p, pn) Mo^{99} reaction, i.e., the deposit thickness would have to be several milli-inches. Molybdenum has very high melting (2620 ± 10 °C) and boiling (4507 °C) points, thereby making it impossible to use the conventional vapor deposition techniques. It should, however, be possible to make use of thermal cracking of certain molybdenum compounds to make good, thick, molybdenum targets. It is the purpose of this report to describe a technique of making thick molybdenum targets using the thermal cracking process.

EXPERIMENTAL PROCEDURE

Thermal cracking involves breakup of the "low" temperature molecules in contact with a "hot" surface in an inert atmosphere. (The terms "low" and "hot" are used only in the comparative sense.) If one of the molecular constituents is gaseous after decomposition, it flies off on breakup, leaving the metal atom(s) behind on the hot surface. If the hot surface is atomically clean, the metal atom sticks to the hot surface by a strong interatomic bond. In the following paragraphs, a description of molybdenum deposition technique based on thermal decomposition phenomenon is described.

At least two compounds of molybdenum are suitable for thermal cracking. These are $MoCl_5$ and $Mo(CO)_6$. The physical properties of these compounds are summarized in Table I below (ref. 2).

TABLE I.- Physical Properties of $MoCl_5$ and $Mo(CO)_6$

Physical Property	$MoCl_5$	$Mo(CO)_6$
Molecular weight	273.21 amu	264.00 amu
Density	2.928 gms/cc	1.960 gms/cc
Melting Point	194 °C	150 °C (sublimes)
Boiling Point	268 °C	-

In the case of $MoCl_5$, an inert gas like helium is bubbled through its molten bath, mixed with an excess of H_2 gas and allowed to enter the reaction chamber where the substrate to be coated is kept. The combined pressure in the reaction chamber, due to the carrier gas, $MoCl_5$ vapors and

H_2 gas is allowed to rise to 20-30 torr. The substrate is then heated to about 900 °C. At this temperature, the following reduction process occurs at the substrate surface:

$$2\ MoCl_5 + 5\ H_2 \rightarrow 2\ Mo + 10\ HCl \qquad (1)$$

Metallic molybdenum is deposited on the heated substrate.

In the case of $Mo(CO)_6$, the vapors of sublimed $Mo(CO)_6$ are carried by an inert gas into the reaction chamber. The target is then heated to 300-350 °C. At this temperature, thermal decomposition occurs as follows:

$$Mo(CO)_6 \rightarrow Mo + 6\ CO \qquad (2)$$

Metallic Mo is deposited on the heated surface.

In both cases, the total pressure in the reaction chamber should be about 20-30 torr when the target is heated.

It would appear from the above description that it is simpler to vapor deposit molybdenum from $Mo(CO)_6$ than from $MoCl_5$. $Mo(CO)_6$ powder was used as the starting material in the present study.

Target Preparation

Figure 1 shows a photograph of the experimental system used in this study. Figure 2 shows a schematic diagram of the same system. The target A, in the form of a nickel-plated rectangular copper bar with an axial cylindrical hole for a 50-watt heater cartridge, and two plane-parallel aluminum electrodes B(*) are kept inside a bell jar where the pressure is

(*)Aluminum was selected as the rf electrode material because of the fact that it has a lower sputtering rate than any other metal and thus presents little contamination problem (ref. 3).

reduced to about 1 micron with a roughing pump. The bell jar is purged with helium gas twice to remove all traces of O_2 before an rf discharge is struck between the target A and the electrodes B. The presence of oxygen and oil vapors interfere with the deposition of molybdenum atoms on the metal substrate. All necessary care should be exercised to exclude their presence in the reaction chamber. For this reason a liquid nitrogen trap was included between the evaporation chamber and the pump. The rf cleaning process removes all adsorbed gaseous atoms from the target surface to be coated. After about half an hour of rf cleaning, the electrodes B are swung away from the target substrate. The target is heated, with the help of the heater cartridge inside the target bar, to a temperature in the range 300-350 °C as indicated by a thermocouple attached to it. The bell jar pumping valve is closed and the flask containing the $Mo(CO)_6$ is heated.(*) $Mo(CO)_6$ powder vaporizes rather easily at a relatively low temperature of about 150 °C. The $Mo(CO)_6$ vapors are carried by a slow and steady stream of helium into the bell jar. $Mo(CO)_6$ decomposes as it comes in contact with the heated target surface, leaving Mo deposit on the target. Carbon monoxide gas is left in the jar as a byproduct. Excellent Mo-substrate bonding is obtained by this technique. When a coating of desired thickness, determined by the amount of $Mo(CO)_6$ used and the heated target surface area, has been deposited, the current through the target heater cartridge is stopped and

(*)Five grams of $Mo(CO)_6$, for target substrate area of 100 cm^2, were used to obtain approximately half a mil thick molybdenum deposit. The amount of $Mo(CO)_6$, of course, depends on the thickness of the molybdenum deposit desired.

the target is allowed to cool to the room temperature slowly to avoid any molybdenum deposit "buckling" due to differences in the thermal properties of molybdenum and the substrate material.

Using the above technique, it has been possible to make "thick" natural molybdenum deposits of good quality on nickel plated, as well as pure, copper substrates. The deposit quality stayed good when a second coat of vapor deposit was applied to the target after exposure to room environment. The target was rf cleaned, in the same manner as before the application of the first coat of molybdenum deposit, before the second deposit was made.

CONCLUDING REMARKS

In the present experimental arrangement, the $Mo(CO)_6$ target material was kept in a flask outside the reaction chamber. The $Mo(CO)_6$ vapors had to be transported to the reaction chamber by about 1-foot length of teflon tubing. This has resulted in the efficiency of molybdenum deposition of the order of 50 percent only, i.e., only about 50 percent of Mo in the $Mo(CO)_6$ compound did get deposited on the target substrate, owing to condensation on the flask and tubing walls. If a greater deposition efficiency is required, as might be the case when a costly separated isotope like Mo^{100} - which costs about $2000/gm - has to be vapor deposited, it would be advisable to use an internally located tantalum boat to hold the $Mo(CO)_6$ powder. The boat can be shielded from the target substrate when the substrate is being heated to avoid premature $Mo(CO)_6$ vaporization. After the target substrate temperature has been raised to the desired value, the boat holding the

$Mo(CO)_6$ can be raised up and heated to evaporate $Mo(CO)_6$. By a proper choice of the substrate target size and the location of boat relative to it, the efficiency of molybdenum deposition can be raised to 90 percent or even higher. Figure 3 shows a schematic representation of such a vapor deposition system.

There seems to be a strong correlation between the oxygen and the carbon vapor content of the reaction chamber and the quality of the molybdenum deposit. Proper care should be exercised to avoid any oxygen and carbon (oil vapor) contamination during the deposition process.

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APPENDIX 1

Potential Technology Application Report

RTI/VAM-15

"Cooling of Metals Under Electron Bombardment"

Mr. Joe E. Beaver, Director
Cyclotron Unit
Department of Nuclear Medicine
University of Miami
Miami, Florida

Team Member - R. W. Scearce

Problem Acquired - June 1973
Potential Technology Application Identified - March 1974
Elapsed Time - Twenty-one Months

Description of Problem

The Department of Nuclear Medicine at the University of Miami has a cyclotron installed at its Mt. Sinai Medical Center. One benefit derived from this cyclotron is the ability to produce the radioactive materials used in their clinical and medical research operations. Fortunately, a similar benefit is extended beyond the bounds of the Medical Center to all of central and south Florida. Medical personnel of that area now have ready access to many previously unavailable medically important radioactive materials. This means not only added capability to the doctor, but the patient benefits through lower costs, shorter treatment times, and lower radiation levels.

Cyclotron production of many important tracer materials is accomplished by bombarding specific metals with a high intensity electron, or proton beam. This bombardment will cause extremely high temperatures to exist in the metal. The rate at which this heat can be dissipated is a limiting

factor in this type of cyclotron application. In order to maximize the heat dissipation, the metal to be bombarded is deposited on a small piece of oxygen free copper called a target. This target is an integral part of a cooling system through which chilled water is pumped at a high volume rate. Thus, the bond between the metal and the target must be both a good thermal bond and a mechanically strong bond.

There is a continuing search for new techniques for producing medically useful radioactive materials on a cyclotron. With each additional technique, there is a two-fold benefit. First, medical research and clinical personnel have the added capability provided by the additional radioactive material. Secondly, if the cyclotron is operated on a cost sharing basis, the operating efficiency of the cyclotron is increased thus reducing production costs.

An important radionuclide which is finding growing applications in the medical community is Technitium-99m. If Technitium-99m could be cyclotron produced, its availability would be greatly increased. In addition, its sale would provide a major revenue source to offset cyclotron operating expenses. (It has been estimated that the Technitium-99m used by Mt. Sinai Hospital alone would provide the cyclotron unit in excess of $30,000 per year additional income.)

The problem originator has demonstrated the feasibility of producing at substantially less cost commercial quantities of this nuclide on a cyclotron. He bombards the stable isotope molybdenum-100 with a proton beam. Following the bombardment, the Technitium-99m is isolated by chemical processes from the molybdenum. Since the production of the Technitium involves only a tiny loss of molybdenum-100, the molybdenum-100 is reclaimed

and reused. This is extremely critical in the process because the molybdenum-100 cost $1750 per gram. Unfortunately, the problem originator has been unable to find an acceptable method for depositing the molybdenum-100 on the copper target. The only known methods, vacuum deposition and sputtering, are known to cause sizeable losses of the material being deposited. Some technique is needed which is simple, not too expensive, and can efficiently deposit molybdenum-100 on copper and provide a strong mechanical bond and good thermal bond between the copper and the molybdenum.

Description of Potential Solution

Through the efforts of Mr. John Samos, Technology Utilization Officer at LRC, this problem was brought to the attention of Dr. Jag J. Singh, Staff Scientist of the Instrumentation Research Division at LRC. Dr. Singh is a physicist with extensive experience in material deposition techniques especially as they apply to preparation of cyclotron targets. After studying the molybdenum-100 deposition problem, he suggested using a recently developed vapor deposition process in which the material loss problem has been largely eliminated. However, this new technique requires a compound of molybdenum rather than the basic element. He suggested either molybdenum pentachloride or molybdenum hexacarbonyl.

The basic process is a vacuum deposition process in which the molybdenum compound is vaporized by heating. The resulting vapors fracture upon contact with a heated surface into molybdenum and a gaseous residue. The molybdenum is deposited on the heated surface and the gaseous residue is removed through the vacuum system. The area covered by the molybdenum can be further

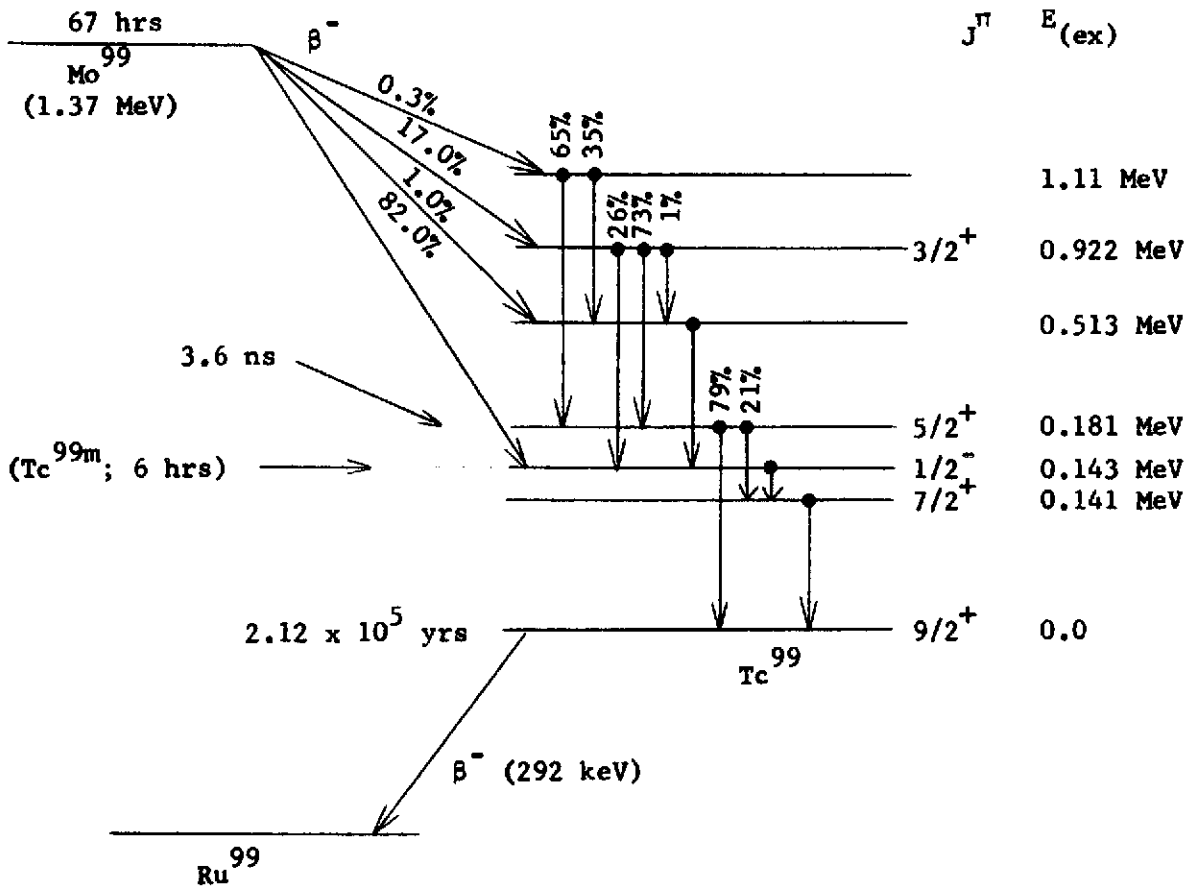
restricted through simple shielding techniques. With shielding and the fact that the compound fractures only on a heated surface, losses are reduced to near zero. The extreme temperature (upwards to several thousand degrees C) associated with depositing molybdenum are not required with many of the molybdenum compounds. As an example, in the suggested vacuum deposition process, molybdenum hexacarbonyl vaporizes at 150°C and the target must be at 350°C. This is a significant advantage of the proposed process since equipment cost and complexity are both significantly reduced.

The suggestion was discussed with the problem originator. He indicated that there was no problem in obtaining the molybdenum-100 in the necessary compound form. During the ensuing discussion, the process using molybdenum hexacarbonyl was agreed upon as the most acceptable, and a program was designed to evaluate the proposed solution. Using a furnished copper target, Dr. Singh would prepare the molybdenum coated target. The problem originator would install the target in the Mt. Sinai cyclotron and subject it to a proton beam. He would also perform the necessary chemical analysis to isolate the Technitium-99m. The coated target will be ready for delivery to Mt. Sinai Hospital by early July 1974.

APPENDIX 2

DECAY SCHEME OF Mo^{99} (Ref. 1)

Mo^{99} can be prepared by the reaction Mo^{100} (p, pn) Mo^{99} in a cyclotron. Mo^{99} decays to the Tc^{99} according to the following scheme.



It is the 6 hours half-life Tc^{99m} isomer that serves as the radionuclide of interest in medical trace studies. Tc^{99m} is finding increasing use in medical work because of its tendency to concentrate in tumorous tissues.

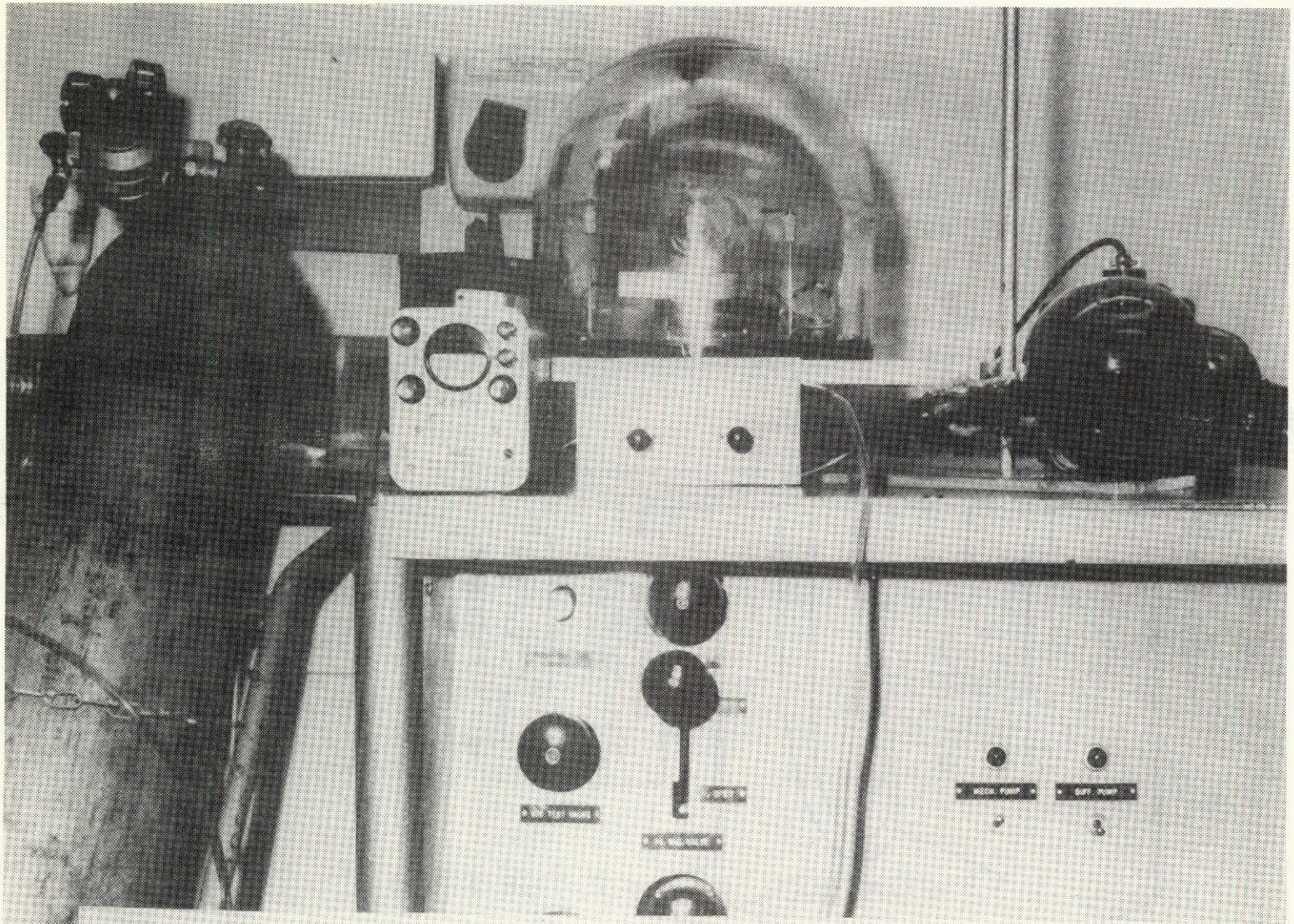


FIGURE - I. PHOTOGRAPH OF THE EXPERIMENTAL SET-UP USED IN THE PREPARATION OF THICK MOLYBDENUM TARGETS.

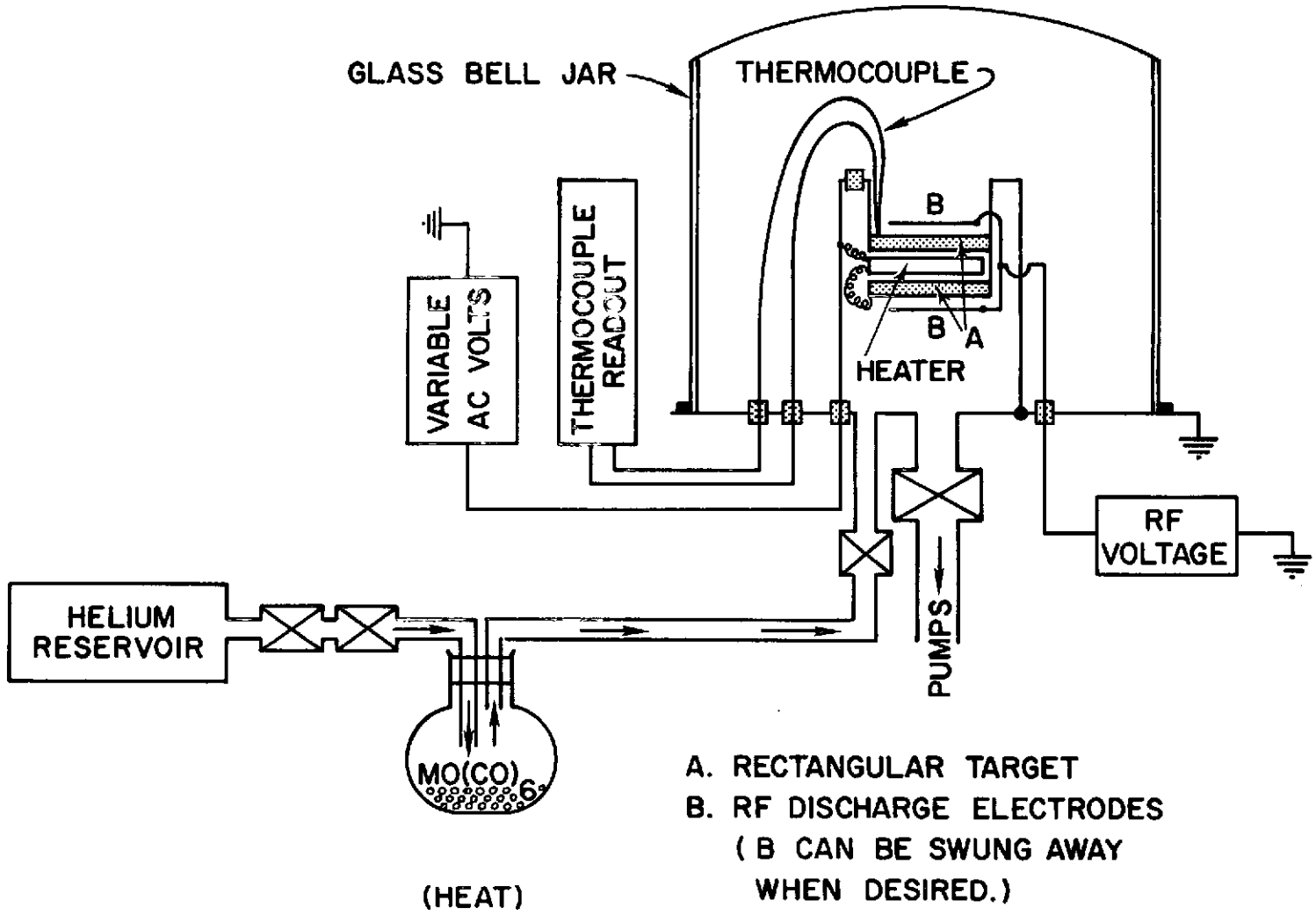
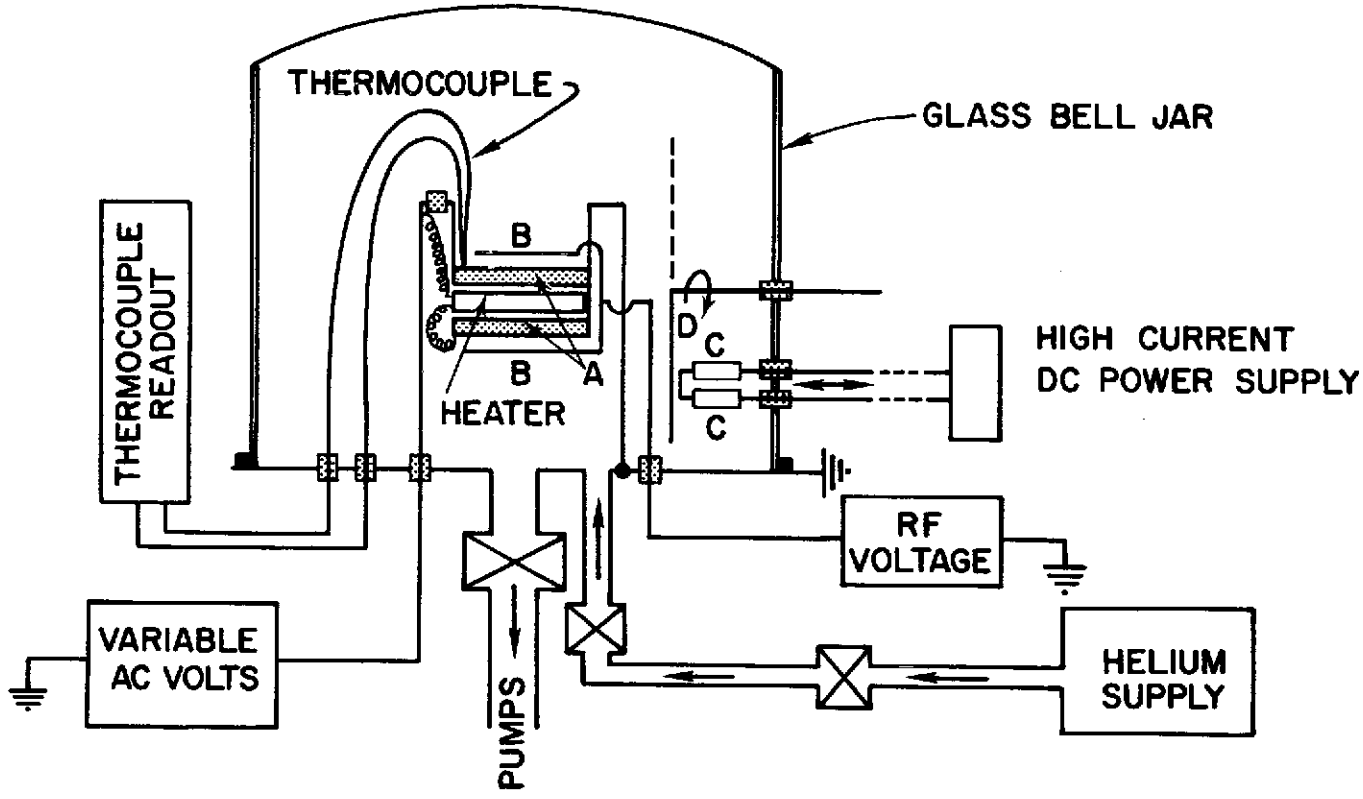


FIGURE-2. SCHEMATIC DIAGRAM OF THE EXPERIMENTAL SET-UP USED IN THE PREPARATION OF THICK MOLYBDENUM TARGETS.



A. RECTANGULAR TARGET TO BE COATED

B. RF DISCHARGE ELECTRODES

C. TANTALUM BOATS HOLDING $MO(CO)_6$ POWDER

D. THERMAL SHIELD

FIGURE-3. SCHEMATIC DIAGRAM OF THE SUGGESTED EXPERIMENTAL SET-UP FOR INCREASING MOLYBDENUM VAPOR DEPOSIT EFFICIENCY.