LA-2439

LOS ALAMOS SCIENTIFIC LABORATORY
OF THE UNIVERSITY OF CALIFORNIA ○ LOS ALAMOS   NEW MEXICO

PREPARATION AND FABRICATION OF
PLUTONIUM FUEL ALLOY FOR LOS ALAMOS
MOLTEN PLUTONIUM REACTOR EXPERIMENT NO. 1

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by

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ABSTRACT

Tantalum-sheathed plutonium fuel pins have been prepared for the first core loading of the Los Alamos Molten Plutonium Reactor Experiment-I. Plutonium-10 atomic percent iron alloy was prepared by co-reduction and by co-melting methods. After casting the alloy into rods, each rod was machined and finished to a 0.557 in. dia. piece weighing 175 g. The finished alloy rod was finally placed in a tantalum sheath, then sealed by fusion welding to a tantalum cap. Procedures and equipment used for alloying, casting, machining, welding and inspection are described. Methods used to prepare rods of other low melting plutonium alloys also are discussed.

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INTRODUCTION

The Los Alamos molten plutonium reactor program is based on the utilization of liquid plutonium as a fast breeder fuel which operates at approximately 600°C.[1] Such low melting fuels are now limited to alloys that contain no fertile material, thereby restricting the reactor to a two-region breeder. In order to keep the critical mass of the core small in the first reactor experiments, a high concentration of plutonium is desired in the fuel. The alloys tabulated below have been considered.

Table 1

Low Melting Alloys Suitable for Molten Plutonium Fuels

Alloy	Solidus point, °C
Pu-9.5 a/o Fe	409[2]
Pu-12 a/o Co	405
Pu-12.5 a/o Ni	465
Pu-Ce-12 a/o Co	< 450°C

The cobalt ternary alloy has the advantage that the plutonium concentration can be varied (at the expense of cerium) from 20 to 88 atomic percent with only a small increase in the solidus point temperature. However, for LAMPRE-I, it was necessary to specify the fuel composition before the plutonium-cobalt-cerium phase diagram was known in detail in this region. On the basis of metallurgical information available at that time, the plutonium-iron alloy was chosen.

The first core for LAMPRE-I will consist of approximately 150 rods nominally 0.36 in. dia. by 6-1/4 in. long, contained in a tantalum capsule of 0.025 in. wall thickness. After insertion in the core, the plutonium alloy will be melted.

Methods that were used to prepare, cast, machine, sample, and encapsulate the plutonium-iron fuel are described in the following sections. Methods for preparing some of the other alloys shown in Table 1 also are described. These alloys were cast, machined and encapsulated by the same methods used for the plutonium-iron alloys.

PREPARATION OF ALLOY

Methods used to prepare plutonium metal as a regulus from plutonium nitrate solution have been reported previously.[3,4] Plutonium was precipitated as plutonium peroxide, which was then filtered, washed, and dried. The peroxide cake was then reacted at 600°C with hydrogen fluoride to form plutonium(IV) fluoride. This fluoride powder was mixed with iodine "booster" (0.1 mole iodine per mole plutonium), and with a 25 percent excess of calcium metal (-10 +40 mesh, U.S. Standard sieve size). The mixture was poured into a magnesia crucible which was contained in a steel reduction bomb. The annular space between crucible and bomb was packed tightly with magnesia sand to prevent fracture of the crucible by thermal shock, and to improve insulation of the charge. After the reduction bomb had been filled with argon, it was heated in an induction coil to initiate the following reactions:

$$Ca + I_2 = CaI_2$$

$$PuF_4 + 2Ca = 2CaF_2 + Pu$$
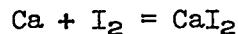
After reduction, the bomb was disassembled and the plutonium recovered as a regulus at the bottom of the magnesia crucible. This product was then pickled in concentrated nitric acid, washed with water, and dried.

Plutonium metal of 99.8 percent purity can be produced routinely at 99 percent yield by this method in the plant.[3]

Plutonium-iron alloy was prepared by mixing coarse iron filings with the plutonium tetrafluoride before the reduction step.[5] The iron concentration in the resulting regulus was predictable within 0.04 atomic percent.

Other plutonium alloys also have been prepared by alloying in the reduction step. Generally these preparations have been used for metallurgical studies on other liquid fuel systems. Plutonium-2.34 to 7.83 a/o aluminum, plutonium-12.0 a/o cobalt, and plutonium-12.5 a/o nickel alloys have been prepared by this method.

Attempts to prepare plutonium-75 a/o cerium alloys by mixing cerium(IV) fluoride with the plutonium(IV) fluoride and reducing with calcium resulted in a porous regulus having an unpredictable concentration of cerium.[5] Excellent results were obtained, however, when plutonium(IV) fluoride was reduced with molten cerium-cobalt alloy at 800°C.

Plutonium-cerium alloys, as well as plutonium-cerium-cobalt alloys have been prepared by co-melting in a dual frequency induction furnace. For example, the ternary alloy has been prepared in this manner from binary plutonium cobalt alloy. The appropriate amount of cerium was added to the binary plutonium cobalt alloy in a tantalum crucible. The tantalum crucible was previously coated with a thin (< 0.001 in.) layer of suitable ceramic to prevent wetting and interaction with the melt. The ingredients were then heated to 750°C by means of a motor-generator set having an output frequency of 10 kilocycles per second. On reaching 750°C, the power supply to the induction furnace was transferred from the motor-generator to a 60 cycle per second supply to provide stirring of the melt. The 60 cycle supply is insufficient to maintain the melt at a high temperature on the 3 kg. scale. Therefore, when the melt temperature had dropped to 600°C, the power supply was switched back to the motor-generator set. By operating the furnace in this manner, uniform ternary alloys have been produced within 15 minutes on the 3 kg. scale. Binary plutonium-cerium alloys also have been produced by the dual frequency method. However, for cerium-rich alloys a temperature of 850°C was required.

After alloying in the coated tantalum crucible, the alloy can be recovered quantitatively by simply dumping it from the crucible.

CASTING OF ALLOY INTO RODS

Generally the alloy reguli and recycled scrap were remelted and cast into rods on a 5-kg. batch scale. The feed metal was loaded into a ceramic melt crucible, which was then placed in a vacuum induction furnace. A mold suitable for casting 19 rods simultaneously was positioned directly below the melt crucible.

The melt crucible was approximately 3-in. in dia., and 9-in. long. A 0.37-in. dia. pouring hole, located in the hemispherically shaped bottom of the crucible, was plugged by means of a plutonium-iron alloy conical plug. (After melting the crucible charge, the induction coil can be lowered to melt this plug also, thereby effecting a pour.)

A drawing of the casting mold is shown in Fig. 1. The mold is made of graphite and coated with a thin layer of ceramic. The bottom section of the mold is removable to provide access to both ends of the mold for coating.

The separable bottom also facilitates machining of small V grooves (0.031 in. wide by 0.015 in. deep) which provide flow channels that connect each tube of the mold. This insures a uniform filling of all tubes. A photograph of the mold is shown in Fig. 2.

The procedure for remelting and casting the alloy was quite simple. First the mold, crucible (containing the alloy), radiation shield, thermocouple bell jar, and induction coil were placed in position as shown in Fig. 3. The inside of the bell jar was evacuated, and the casting mold was outgassed at 400°C. The charge in the melt crucible

27/64 DIA. 19 HOLES

3 7/8

2 5/8

1 3/8

9 1/2

1 1/8

CERAMIC
COATED
SURFACES

GRAPHITE
ROD MOLD

GRAPHITE
BASE

3/8 SOCKET HD. CAP SCREW
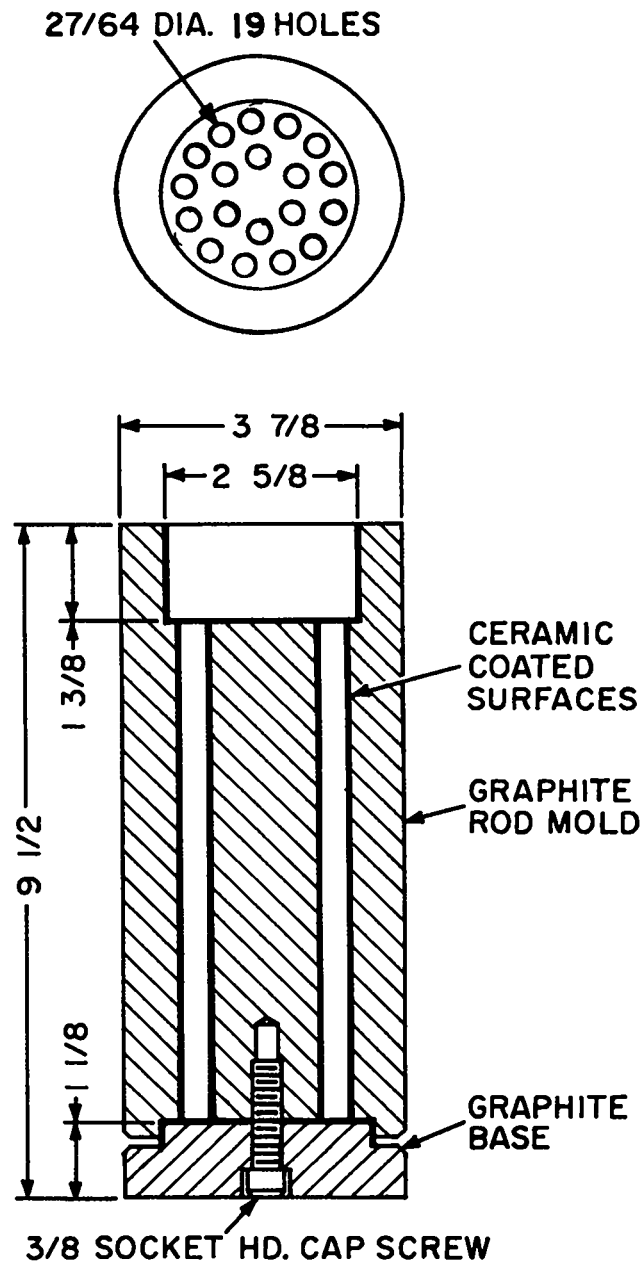
Fig. 1.   Schematic diagram of casting mold.

Fig. 2. Photograph of casting mold.

THERMOCOUPLE — PYREX BELL JAR
FEED MATERIAL — INDUCTION COIL
CERAMIC RADIATION SHIELD — MELT CRUCIBLE
COOLING COILS — SPACER
GRAPHITE ROD MOLD — INDUCTION COIL
TO DIFFUSION PUMP
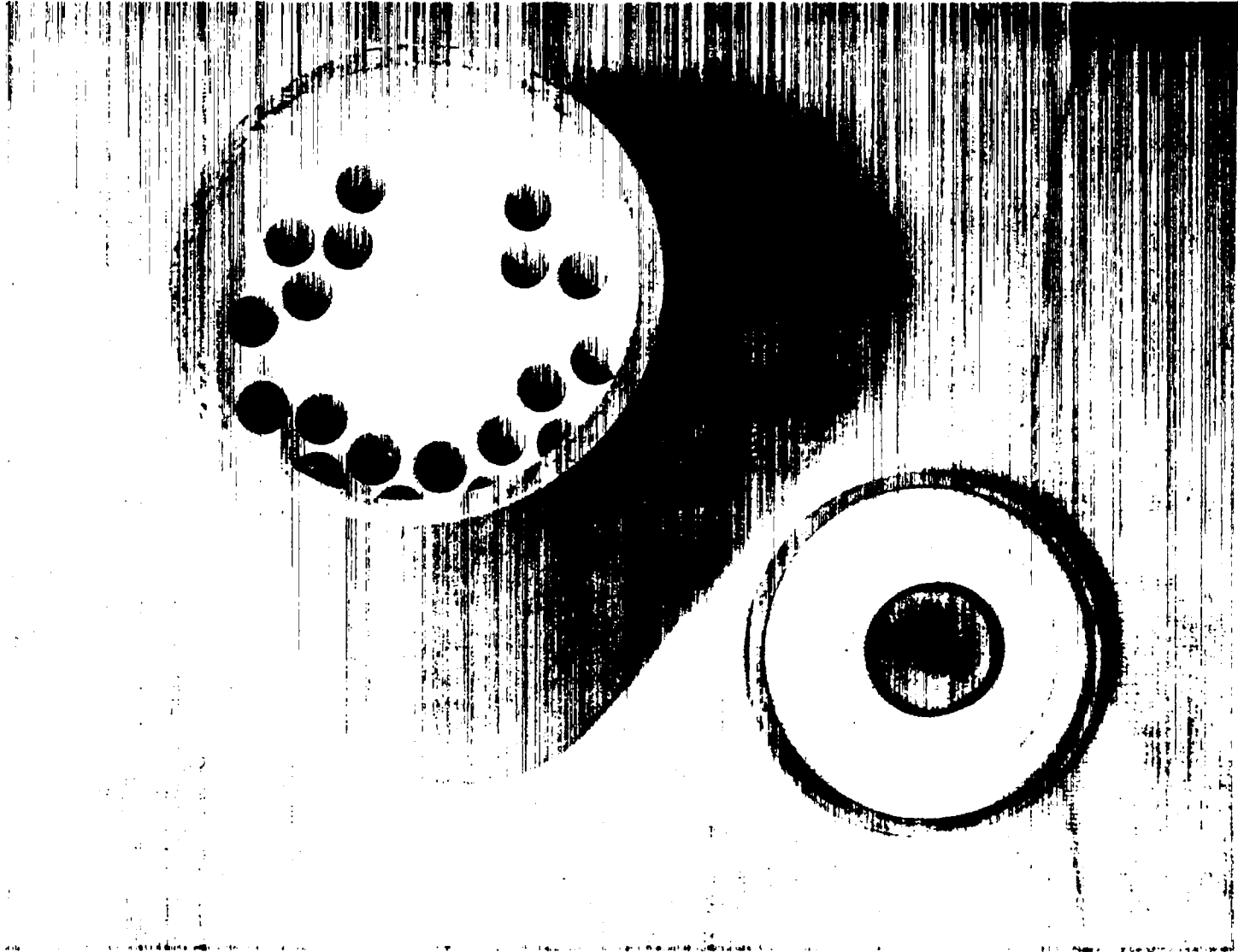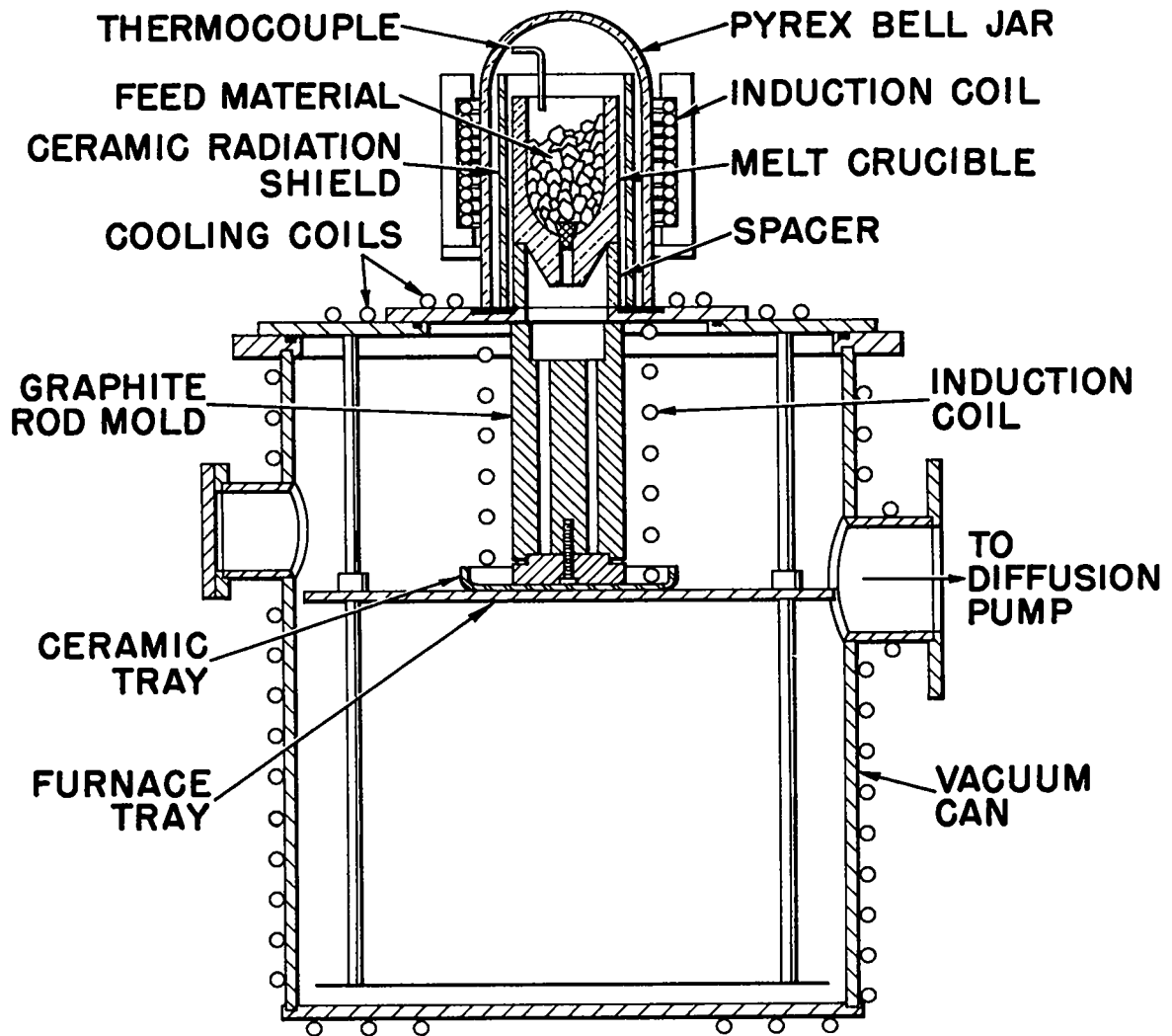CERAMIC TRAY
FURNACE TRAY
VACUUM CAN

Fig. 3. Schematic diagram of melt crucible and casting mold assembly.

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was then heated slowly to 600°C, and held at this temperature until a vacuum of less than 5 microns could be maintained. The melt temperature was then lowered to 525°C and held at this temperature while the induction coil was lowered to melt the crucible bottom plug, thereby causing the melt to flow downward into the casting mold.

The casting and mold were cooled to nearly room temperature, then transferred to a refrigerator and stored at -20°C overnight. The alloy rods must be kept in the mold during the cold cycle to prevent serious warpage. The rods were removed by dumping from the mold; in some castings it was necessary to break the mold. The mold, melt crucible, and casting skull are shown in Fig. 4. The "as-cast" rods are shown in Fig. 5.

A typical 5 kg. casting produced 97 percent of the plutonium as rods and 3 percent as casting skull.

MACHINING AND SAMPLING

The alloy rods were machined, cropped and sampled in a lathe that had been modified for enclosure in a glove box. Machining of an alloy rod is shown in Fig. 6. The atmosphere within the enclosure was 50 percent (by volume) dry air - 50 percent helium. Pure helium was brought into the enclosure and directed immediately onto the work. (This was adequate to prevent turnings from igniting and produced untarnished alloy rods.) The work was turned at approximately 600 rpm, using carbide-tipped cutting tools such as Kennemetal grade K-6. No
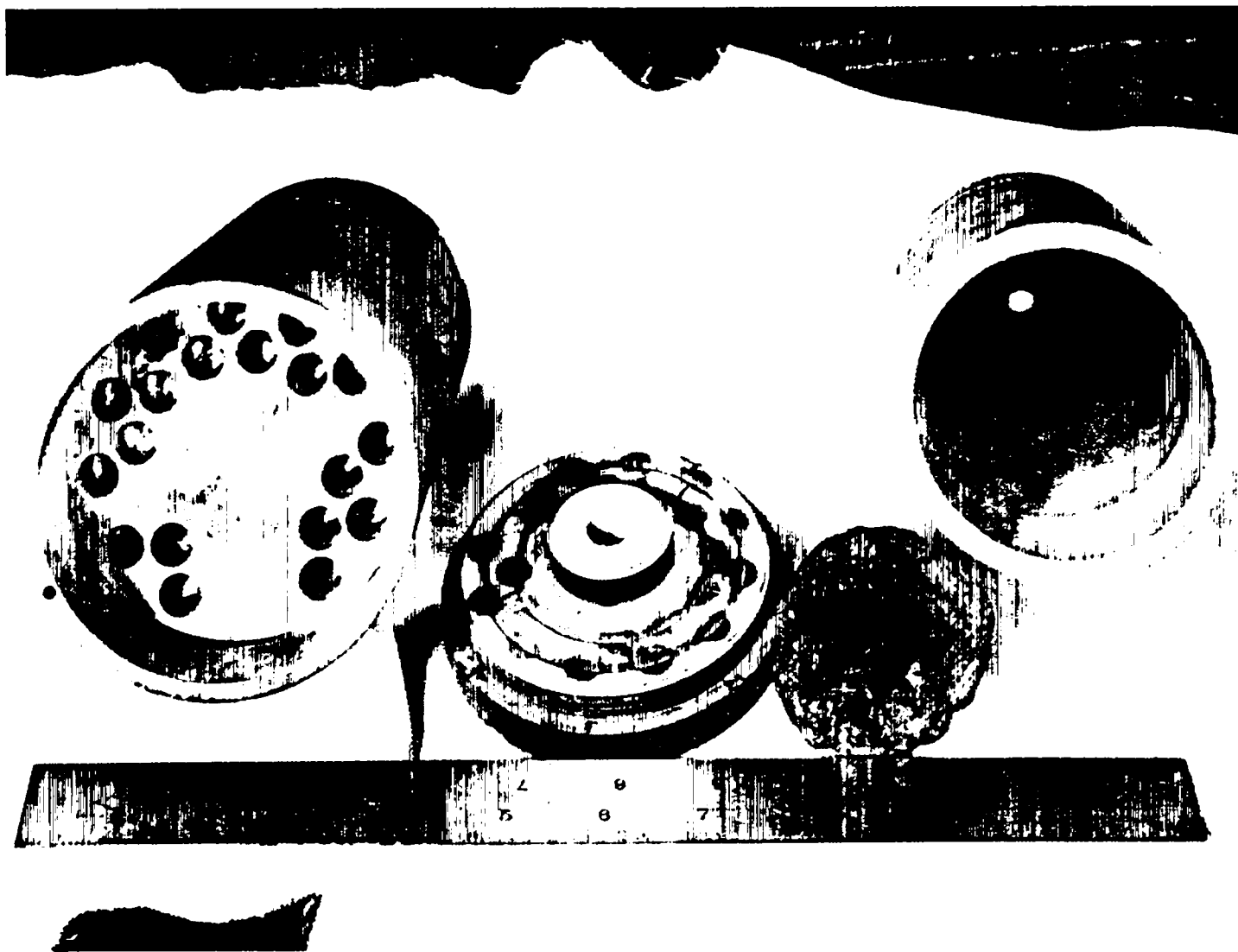
Fig. 4. Photograph of casting mold, melt crucible, and casting skull.
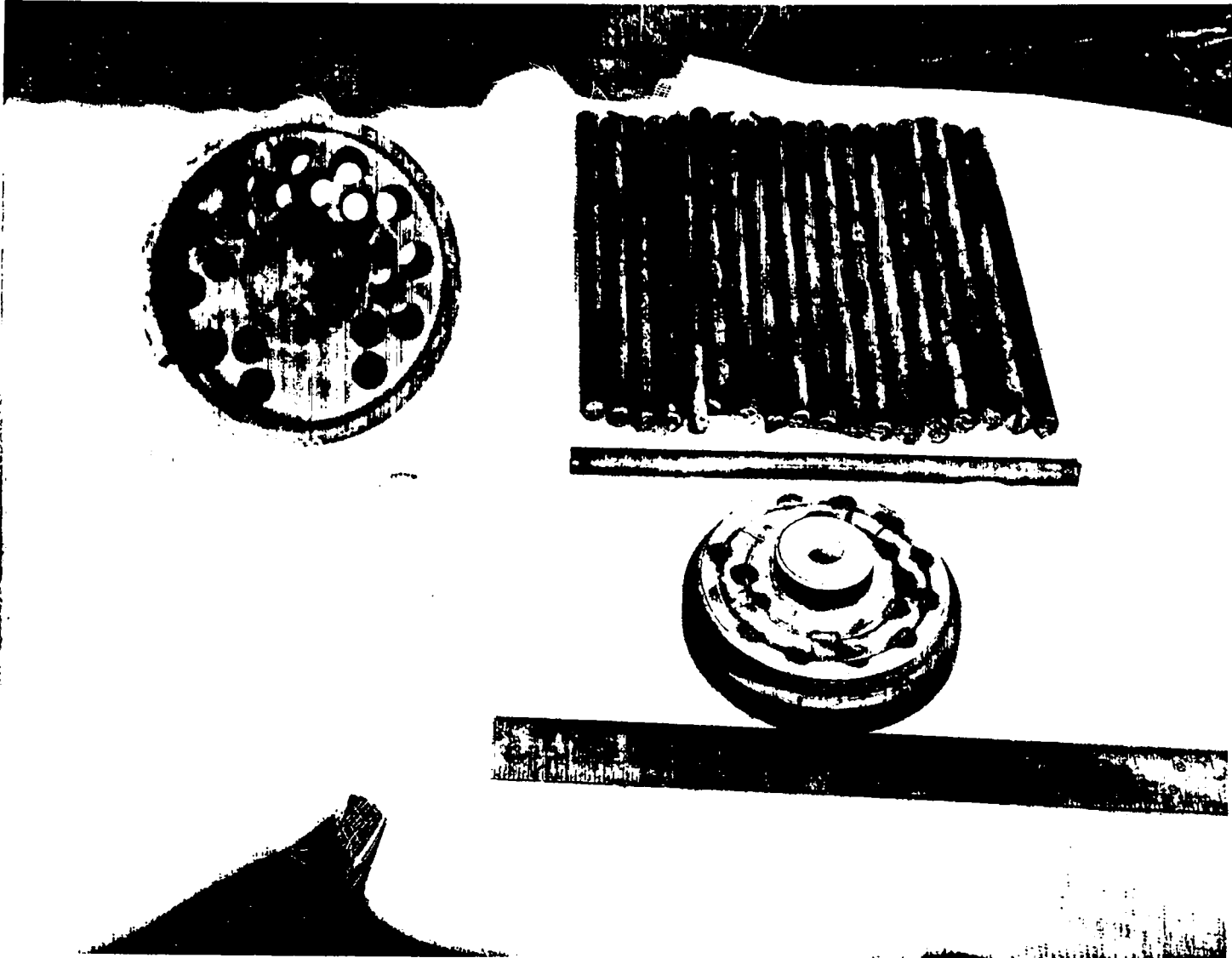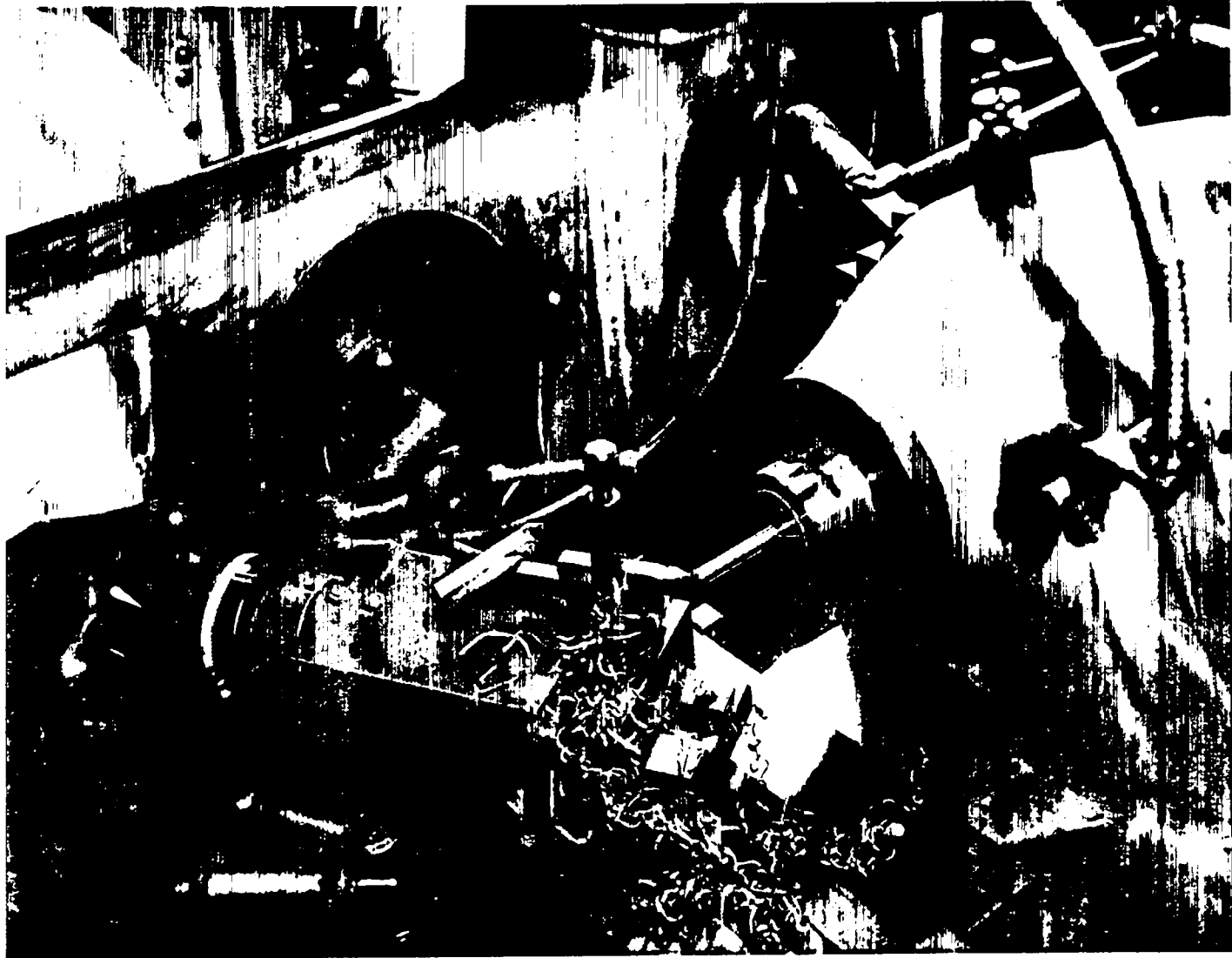
Fig. 5. Photograph of "as-cast" rods.

Fig. 6. Photograph of plutonium alloy rod machining.

cutting lubricant or coolant was used. Alloys of plutonium - 10 a/o iron were very brittle, and machined like cast iron. The plutonium - 13.2 a/o Co-4.6 a/o Ce alloys were even more brittle, and a rod could be shattered by striking a sharp blow. On the other hand plutonium - 20 a/o cerium alloys were very soft, working about like lead.

Each alloy rod was first machined to within 0.01 in. of the final diameter and then sampled for chemical analysis. Approximately 10 g. were required for each hydrogen and each nitrogen determination. A 2 g. disc was required for oxygen analysis, and 5 g. of turnings were required for the remaining analyses. The top 1/2 in. of each rod was not included in the samples; this portion was cropped off and recycled to recover the plutonium. The analytical results on a group of rods are shown in Table 2.

It should be noted that the concentrations of manganese, carbon, and silicon are relatively large. This is intentional, and is due to the use of cast iron, rather than pure iron, in preparing the plutonium-iron alloy. Dynamic corrosion tests conducted by the reactor division have indicated that the use of cast iron greatly reduces corrosion of the tantalum container capsule. For comparison, the impurities are also shown for alloy that was made from high purity iron.

The final machining of the rods was done just prior to encapsulation, in order to minimize oxygen and nitrogen pickup. Each rod was machined to 0.355-0.360 in. diameter, and of sufficient length to weigh 175.0 ± 0.2 g. The exact weight of each rod was determined after encapsulation.

Table 2

Chemical Analysis of Plutonium-Iron Alloy Rods

Element	Plutonium-cast iron alloy		Plutonium-pure iron alloy		
	Rod 1	Rod 2	Rod 3	Rod 4	Rod 5
H	10	10	< 5	10	5
N	6	5	< 5	9	< 5
O	30	50	35	45	30
Mn	400	300	...	...	...
C	290	380	170	245	120
Si	590	570	...	...	...
P	...	...	<10	<10	...
Fe (w/o)	2.40	2.37	2.40	2.44	2.44

The turning chips were recycled back to the rod casting operation.
The cropped end from each rod was dissolved in acid, and the plutonium
was purified and recycled back to the peroxide precipitation step.

ENCAPSULATION OF ALLOY RODS IN TANTALUM

It is important that the deep drawn tantalum tube and end cap,
shown in Figs. 7 and 8, be cleaned thoroughly before welding. They
were subjected to four individual cleaning treatments successively.
First they were degreased with trichloroethylene and dried, then
immersed for 10 min. in cold aqua regia, rinsed with distilled water,
and dried. The cap and weld region of the tube were then cleaned in
a bright-dip solution (55 volumes concentrated sulfuric acid, 25
volumes concentrated nitric acid, and 20 volumes concentrated hydro-
fluoric acid.) After rinsing with distilled water, the parts were
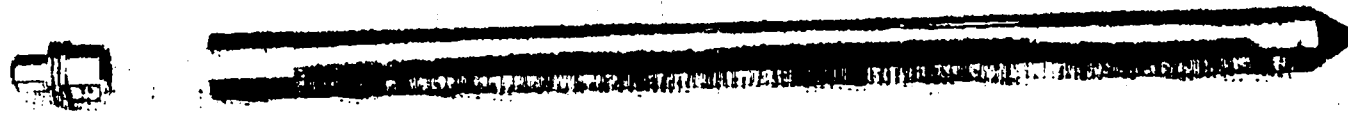
Fig. 7. Photograph of empty tantalum tube and plug.

60°
62°

.060
____ RADIUS
.070

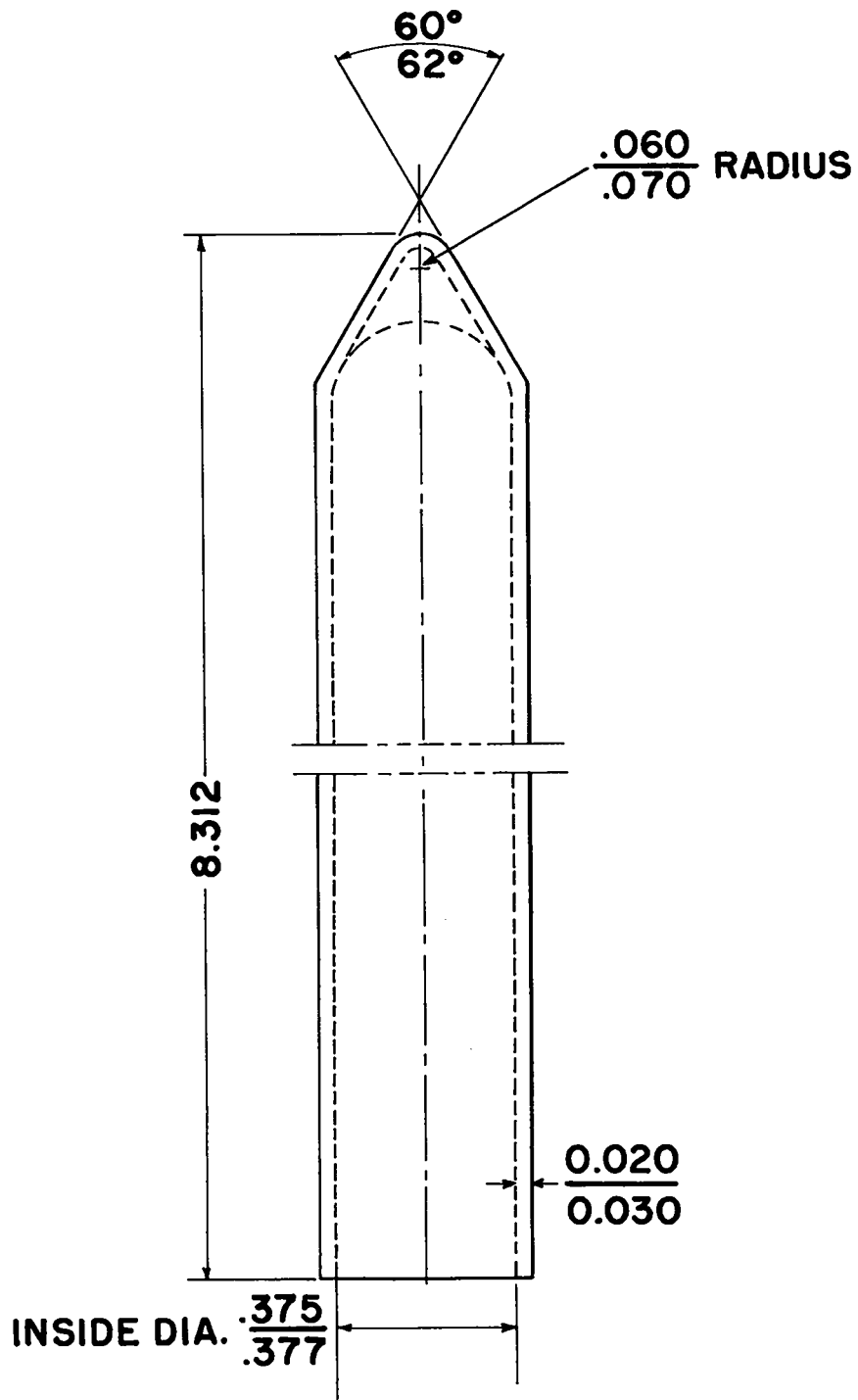8.312

0.020
_____
0.030

INSIDE DIA. .375
_____
.377

Fig. 8. Schematic drawing of tantalum tube.

finally washed with acetone and vacuum dried. The cleaned parts were then weighed before loading with fuel alloy. Handling was done with clean surgical gloves or tissue paper. After weighing, the tube was ready to be loaded with a 175 g. alloy rod.

The plutonium alloy rod, after finish machining, was cleaned with carbon tetrachloride and placed in a transfer tube that had been flushed and filled with argon. The end of the transfer tube was sealed by a rubber stopper, as shown in Fig. 9. The plutonium alloy rod was then transferred to the terminal glove box enclosure, which is adjacent to a temporary welding hood. A sliding door between the enclosure and the hood permits the air transfer of the plutonium alloy.

The welding unit is shown schematically in Fig. 10. The welding chamber consists of a lucite tube 8-in. dia. by 15-in. long, closed at the top by a dural lid and at the bottom by a dural base plate. The fuel capsule was held in a heavy copper collet which slips into a brass tube. In addition to serving as a heat sink, the brass tube can be rotated to turn the collet and tantalum capsule. The rotational speed can be varied by means of a variable speed gear reduction motor which drives a coupling shaft through a rotary vacuum seal. A tungsten electrode is mounted through a bellows seal, and passes radially into the welding chamber. The chamber is connected to helium, argon and vacuum lines, with appropriate gauges and valves, to provide an inert atmosphere. A mercury bubbler in the exhaust gas line controls the chamber at a pressure that is slightly greater than one atmosphere. Mounted through

Fig. 9. Photograph of transfer tube.

CAP INSERTION ROD

WELDING CHAMBER

CYCLE CONTROLLER

TUBE HOLDER

HELIUM ARGON

ADJUSTABLE ELECTRODE HOLDER

WELDING CHAMBER

VACUUM

AC-DC WELDER

GAS EXHAUST

MERCURY BUBBLER
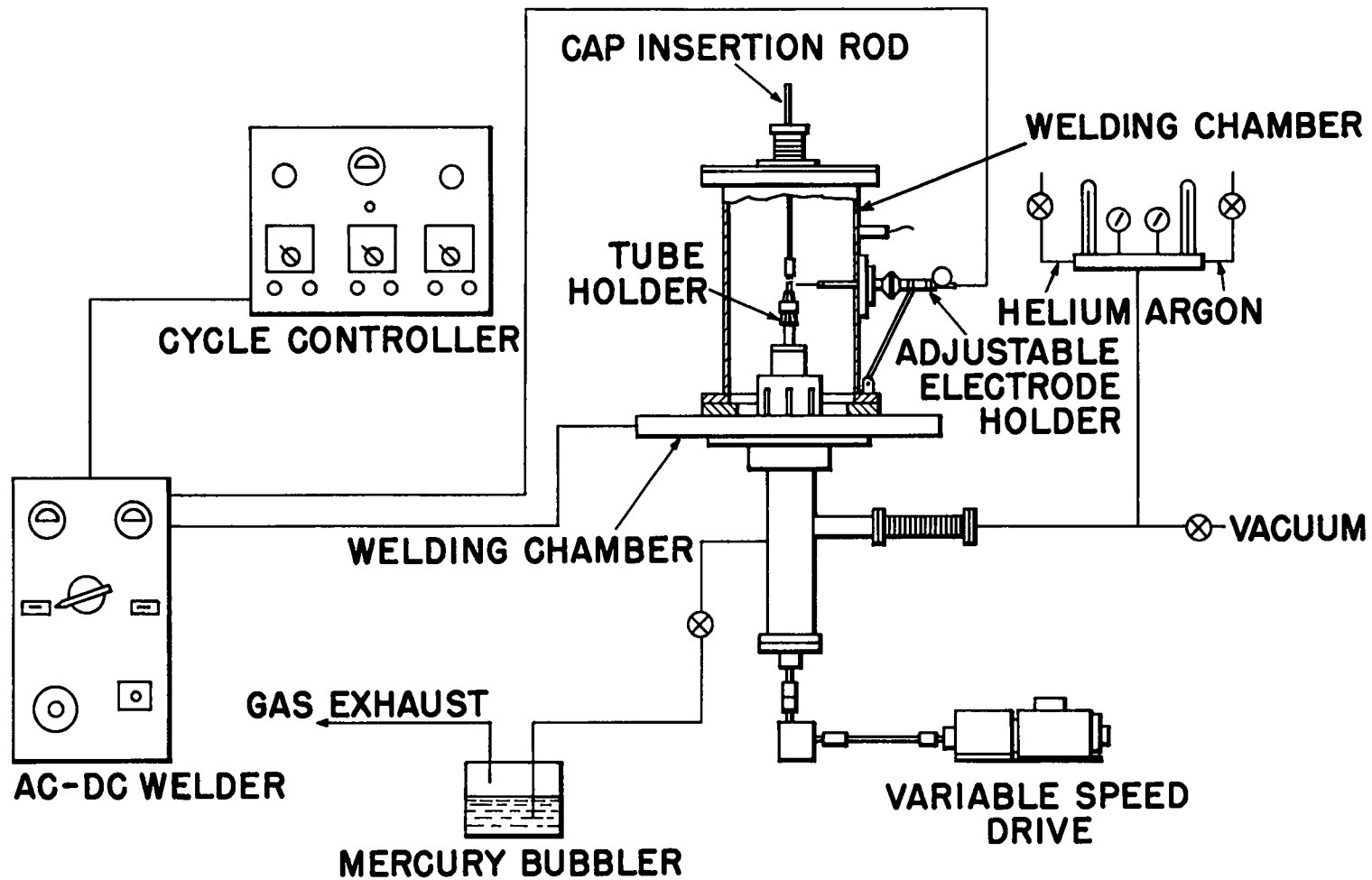
VARIABLE SPEED DRIVE

Fig. 10. Schematic drawing of welding unit.

the center of the chamber lid is a rod which holds the tantalum cap.
The rod is sealed to the chamber lid through a bellows. The lower end
of the rod contains a small neoprene "O" ring for holding the tantalum
cap in place until the welding chamber is purged with inert gas. This
rod may be lowered to insert the cap into the tantalum tube.

The welding power supply was a 300 KW AC-DC rectifier with a built
in automatic high frequency unit for starting the arc. The caps were
welded to the tantalum tubes at about 50 amperes direct current at 12
volts, using straight polarity. Current adjustment was manually preset
in test welds; the voltage depends on the distance from the electrode
to the work.

The welding time cycle was controlled automatically by a unit which
contained three timers, an "on-off" switch, and indicator lights.
Pressing the "on" switch started the welding and the first timer which
raised the welding current from 0 to the desired value in a preset time.
The second timer then held this current constant for a preset time,
after which the third timer reduced the current slowly to zero to pre-
vent arc-stop pitting of the weld.

In order to load a plutonium alloy rod and tantalum capsule into
the welding chamber, the following procedure was used. The copper collet
and brass tube were removed from the welding chamber and placed in the
hood. A tantalum fuel tube was mounted in the collet, and a thin
tantalum funnel was inserted in the open end of the tube, as shown in
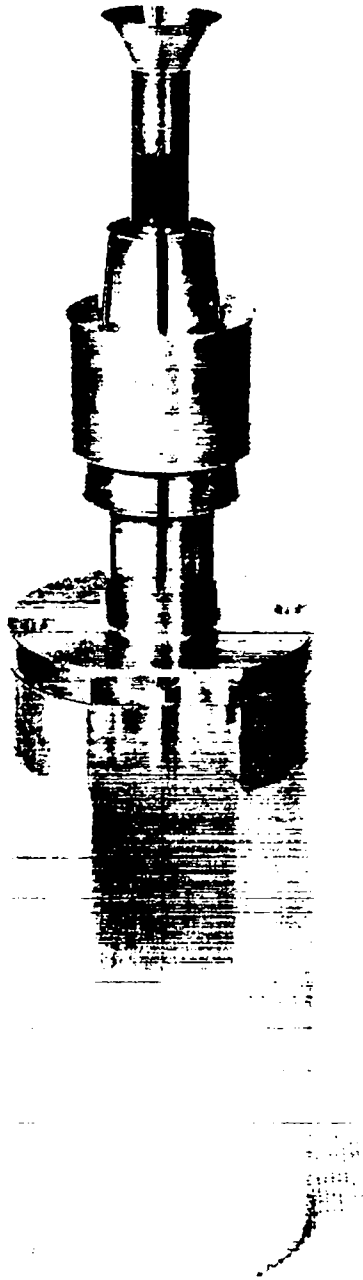Fig. 11. In the glove box next to the welding hood an operator removed

Fig. 11.   Photograph of tantalum funnel and tube held in collet.

the stopper from a fuel rod transfer tube, opened the sliding door between the hood and the glove box, and carefully slid the plutonium alloy rod from the transfer tube onto a piece of cloth in the hood. The rod was then picked up by forceps and dropped through the funnel into the fuel capsule tube. After removing the funnel, the tube holder assembly was mounted in the welding chamber. The tantalum cap was placed on the insertion rod, and the upper lid was then clamped in place. An inert atmosphere was established within the welding chamber by evacuating and refilling with helium twice. Finally the helium flow from the chamber was diverted through the mercury bubbler. At this point the tantalum cap was inserted into the top of the tantalum tube, a small flow of argon was passed into the chamber and the cap was welded to the tube.

In order to weld the fuel capsule, the pointed electrode was positioned about 0.025 in. from the circumferential joint between the cap and tube, in the same plane as the joint. The rotary drive motor was turned on and the time cycle controller was then started. The weld was then completed automatically, under the observation of an experienced welder. After cooling in the inert atmosphere, the weld was inspected visually and monitored for alpha contamination. The assembly was then weighed to determine the exact weight of plutonium alloy. A typical finished fuel rod is shown in Fig. 12.

The finished fuel capsules were finally inspected for leaks by mounting in a vacuum chamber and monitoring for helium with a mass spectrometer leak detector.
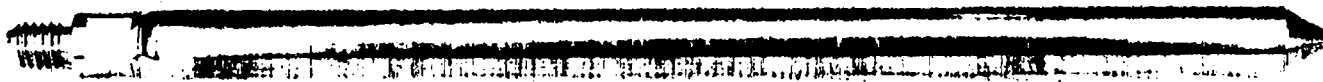
Fig. 12. Photograph of finished plutonium-tantalum fuel rod.

ACKNOWLEDGMENTS

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