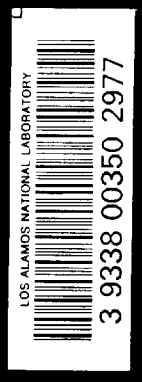

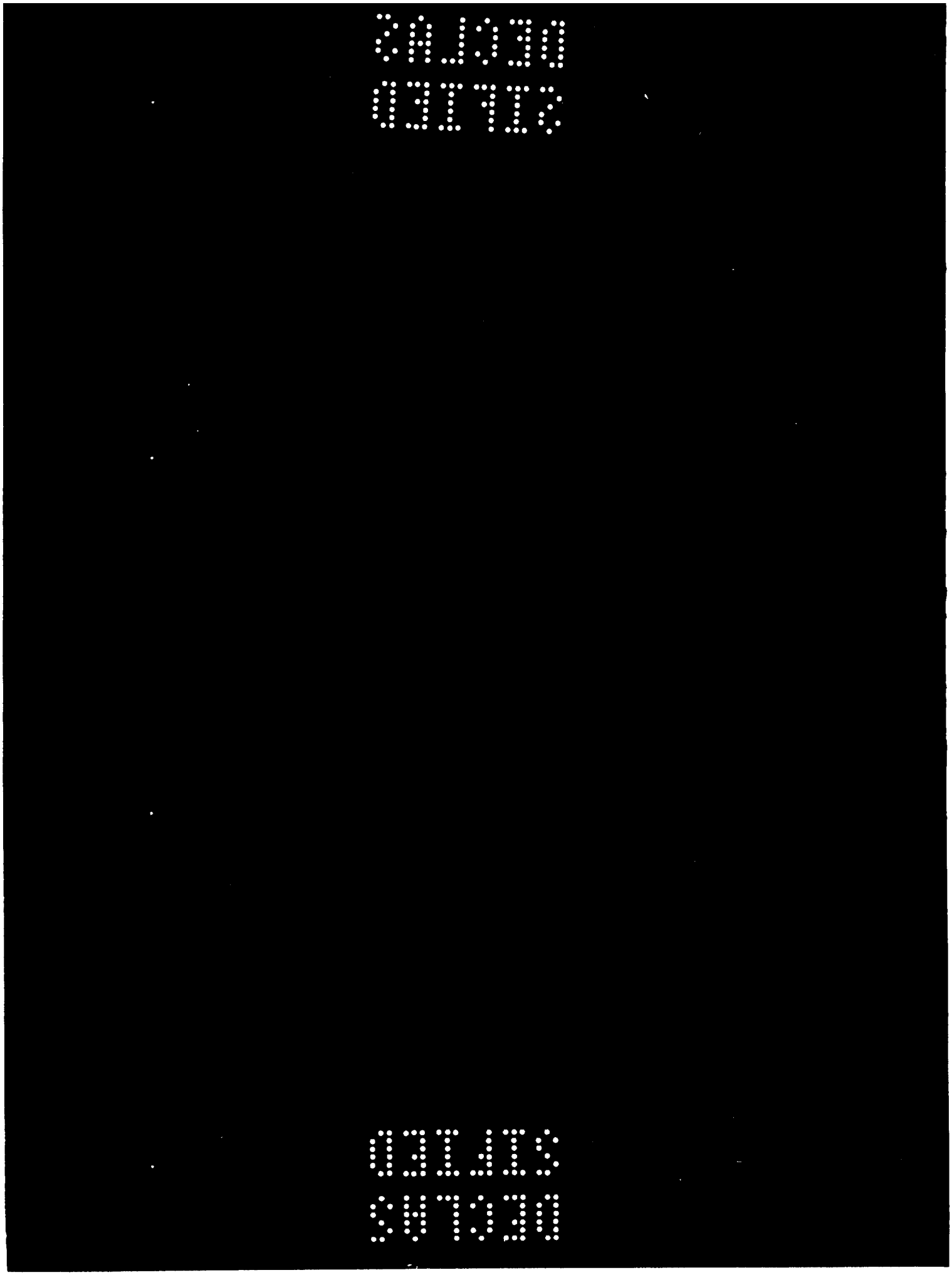

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CHEMICAL AND METALLURGICAL OPERATIONS INVOLVED IN THE FABRICATION OF URANIUM 235 FOR USE IN NUCLEAR WEAPONS: PART III. REDUCTION OF URANIUM TETRAFLUORIDE TO METAL

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ABSTRACT

This report describes the bomb-reduction technique used for the preparation of uranium-235 metal. The method consists, in general, of the reduction of the tetrafluoride with calcium metal. Iodine is used as a "booster" and also to give a more fluid slag. The technique described gives a yield of above 99 percent.

REDUCTION OF URANIUM TETRAFLUORIDE TO METAL

1. Introduction:

Most of the reductions were carried out on the 1000-g scale; the 250-and 500-g scales were used only occasionally. Since the only essential differences are in the size of the bombs and liners used, the 1000-g reduction technique and apparatus will be reported here.

The reaction between a metal halide and an alkaline-earth metal as used in the so-called bomb reduction is of the thermite type. The fundamental requirement for a successful bomb reduction is that a high yield be obtained as a dense, coherent piece of pure metal. The reaction used for the preparation of uranium metal is as follows:

$$UF_4 + 2\ Ca \longrightarrow U + 2\ CaF_2$$

When adapting this reaction to the bomb reduction several fundamental considerations must be studied. The melting points of the products of the reaction and the amount of heat liberated by the reaction are important. It is necessary that the reduction be carried out in such a manner that the products of reaction are in the molten state long enough, and that the slag has a sufficiently low viscosity to allow the metal to collect in a coherent piece. In the reduction of the fluoride with calcium, the combination of the melting points of the products and the heat of reaction is not such as to allow for the best collection of metal. Three possible ways of overcoming this difficulty have been suggested: (a) supply more heat to the bomb by additional external heating; (b) lower the melting point of the slag by the addition of another substance; (c) increase the amount of heat liberated in the charge by having a reaction of high heat take place along with the reduction reaction. It is known that external heating must be carried out at such a rate

that the products of the reaction do not solidify before separation of the metal has taken place. If this does happen it is not possible to collect the metal even at temperatures well above the melting points of the products. The application of very rapid heating of the bomb and its contents is difficult and impractical. In the reduction of uranium tetrafluoride, points (b) and (c) are combined by producing by a con-current reaction a substance which will lower the melting point of the slag while at the same time the reaction supplies additional heat. The reaction used is as follows:

$$I_2 + Ca \longrightarrow Ca + CaI_2$$

The formation of the CaI_2 supplies additional heat to the charge, and the CaF_2 - CaI_2 slag has a lower melting point than the CaF_2 alone. The use of an inert atmosphere, such as argon, in the bomb aids in the separation of the slag from the metal and gives the latter a smooth top. This is probably due to the lowering of the viscosity and /or the melting point of the slag by the elimination of calcium oxide and calcium nitride. If air or nitrogen is used, much of the slag freezes on the liner walls, and the metal button has a poor top which is difficult to clean.

A knowledge of the starting temperatures of the reactions and reaction mixture is important in developing a successful heating or firing procedure. The starting temperatures of the reactions involved have been determined in this laboratory and are given, along with the calculated heats of reaction, in Table I.

TABLE I

Mixture 25 o/o Xs. Ca	Heat of Reaction (ΔH) K cal/mole halide	Starting Temp. ^oC
UF_4 + Ca	-126.0	515°
I_2 + Ca	-128.5	398°
UF_4 + 0.1 mole I_2 + Ca	-138.9	410°

It should be noted that, in addition to supplying more heat and a lower melting slag, the I_2 + Ca reaction determines the starting temperature of the whole reaction. It has been found that variations in the amount of iodine used in the charge does not change the starting temperature.

Another important consideration is the container in which the reaction takes place. This container, usually referred to as the liner, should meet the following requirements:

(a) There should be no reaction between the reducing metal and the liner, or between the products of the reaction and the liner.

(b) The liner should retain the products of the reaction and should be of such purity as not to contaminate the metal produced. The liners used will be discussed in more detail later in this report.

II. Experimental

1. Raw Materials and Apparatus

(a) Raw Materials: The choice of calcium metal used in the thermite reaction under consideration is of primary importance. The reducant must be low in light-element impurities so as not to contaminate the uranium metal produced. It must also be free of oxide and low in nitrogen. It has been found that calcium containing 0.40 o/o N_2 or less is satisfactory for reductions of the tetrafluoride when the bomb is argon filled. The calcium used in the work reported here was redistilled electrolytic calcium manufactured by the Electro-Metallurgical Corporation. The calcium carrots were ground to -3, +4 mesh (1/4" pieces) at Ames, Iowa, and packed in argon for shipment to this laboratory. The calcium was then ground in a Wiley mill and screened, the -20, + 80 fraction being used. This grinding and screening removes much of the oxide and leaves a clean, shiny product. The ground calcium was stored in bottles filled with argon. The analysis of the calcium used is given in Table VI.

TABLE VI

Element	ppm
N_2	400
B	< 0.5
Al	≤ 10
Mn	≤ 10
Mg	< 1000
Fe	50

Reagent-grade, redistilled iodine manufactured by Mallinckrodt Chemical Works was used with no additional grinding. The tetrafluoride used was received as virgin material from Oak Ridge and as recovered material produced by Group CM-16, as described in LA-411.

(b) Apparatus: The apparatus consists, in general, of a bomb, a liner or container for the charge, and a high-frequency converter and coil for heating the bomb. Fig. 1 is a photograph of the bomb, liner, and copper gasket. Fig. 2 is a schematic drawing of the assembled bomb. The screw and gasket in the lid of the bomb is for the purpose of sealing the bomb after filling with argon. The lid has a lip on it which is forced into the annealed copper gasket. The bomb is made of SAE 1020 cold-rolled steel .

The liners used for the reductions reported here were produced at the M.I.T. refractory laboratory. Briefly, the method used is as follows: the electrically fused magnesium oxide powder (2 o/o SiO_2, 200 mesh) is mixed with 7 o/o water and tamped and pressed into steel dies. The formed liner is then extruded from the die, dried, and fired in a gas furnace at 1700° C for three hours. The resultant body is hard and has a porosity of less than 22 o/o. A great deal of empirical development

was necessary before a satisfactory liner was produced. The requirements are strict and hard to specify.

A 20-KW Ajax-Northrup high-frequency convertor with a 9" ID, No. 313 stationary cylindrical furnace was used for heating the bombs. Figure 3 is a photograph of the heating apparatus and hooded cubicle.

2. Reduction Procedure: Respirators and rubber gloves are worn by the operator during the reduction. All operations are carried out in hoods, great care being taken that no material is lost through dusting or spilling. Residues including slag, liners, pickling solutions, etc., are sent to the recovery section.

(a) The charge: The reduction charge consisted of UF_4 + Ca + I_2. The composition of the charge was 0.1 mole of iodine per mole of uranium and 25 o/o excess calcium metal.

(b) Loading of bomb: The liner is placed in the cleaned bomb. The Ca and I_2 are mixed with the fluoride by shaking and rolling the weighed charge in a closed bottle. The reaction mixture is then poured carefully (to avoid dusting) through a nickel-plated funnel into the liner. After placing the refractory lid on the liner, 40-mesh electrically fused magnesia powder is used to fill the space between the liner and bomb wall, and the space above the liner lid and the gasket groove of the bomb. This groove is then brushed free of magnesia and the annealed copper gasket put in place. The bomb lid is then bolted on. A stopcock assembly is then screwed into the hole in the bomb lid and the bomb evacuated. After filling the bomb with argon, the bomb is again evacuated and refilled with argon. The stopcock assembly is removed and quickly replaced with the screw and copper gasket.

(c) Firing the charge: The heating of the bomb and its contents to the starting temperature of the reaction is very important. It has been found by experiment in this laboratory that the charge requires a definite preheat period before the starting temperature is reached. If the bomb is heated rapidly, the reaction starts at the surface of the charge, while the central portions are at a much lower

temperature. In this case more of the heat of reaction is dissipated in heating the charge, thus allowing the products to solidify more rapidly than if a preheat is used. If the preheat period is too long, the calcium particles are coated with a layer of CaI_2 which presumably lowers the rate of reaction with the fluoride. This allows more heat to be dissipated to the liner and bomb before the reaction is complete, thus again causing poor collection of the metal. The heating or firing procedure used here was arrived at by experiment, using several different heating cycles to locate the optimum conditions. When developing a heating cycle, three thermocouples are placed on the inside surface of the liner, one near the top, one at the center, and one on the bottom. The temperature of the liner can then be correlated with the temperature of the outside thermocouple well. It is important that the bomb be located in the coil so that the entire length of the liner heats at nearly the same rate. For example, if at the time of firing the bottom portion of the liner is well below the firing temperature, the metal button is poorly formed and a lower yield is obtained.

In the actual firing procedure used here, the loaded bomb is placed in the 9"-ID induction furnace so that the bottom of the bomb is 1" above the bottom of the coil. The thermocouple (chromel-alumel) is then placed in the well on the bomb and the following heating cycle is followed:

Time (min.)	°C
1	110
2	200
3	280
4	360
5	400
6	425
7	450
8	475
9	500
10	525
11	560
12	575
13	600
14	625
15	650

When the charge reaches the starting temperature, which occurs between 14 and 15 minutes, (outside temperature 625 to 650°) there is a sudden increase in temperature. When this increase occurs, the power is turned off and the bomb is allowed to stand in the coil for about five minutes. The bomb is then removed from the coil and cooled to room temperature in front of a fan.

(d) Unloading the bomb and cleaning the button: After the lid is removed, the outside of the bomb is tapped with a hammer until the contents of the bomb can be poured out. The metal button is then pickled in a 1:3 acetic acid solution to remove any adhering calcium and slag, washed in water, dried with acetone, and weighed. The slag, liner, and solutions are returned to the recovery section. After the bomb is cleaned, it is again ready for use; a new copper gasket is used for each reduction.

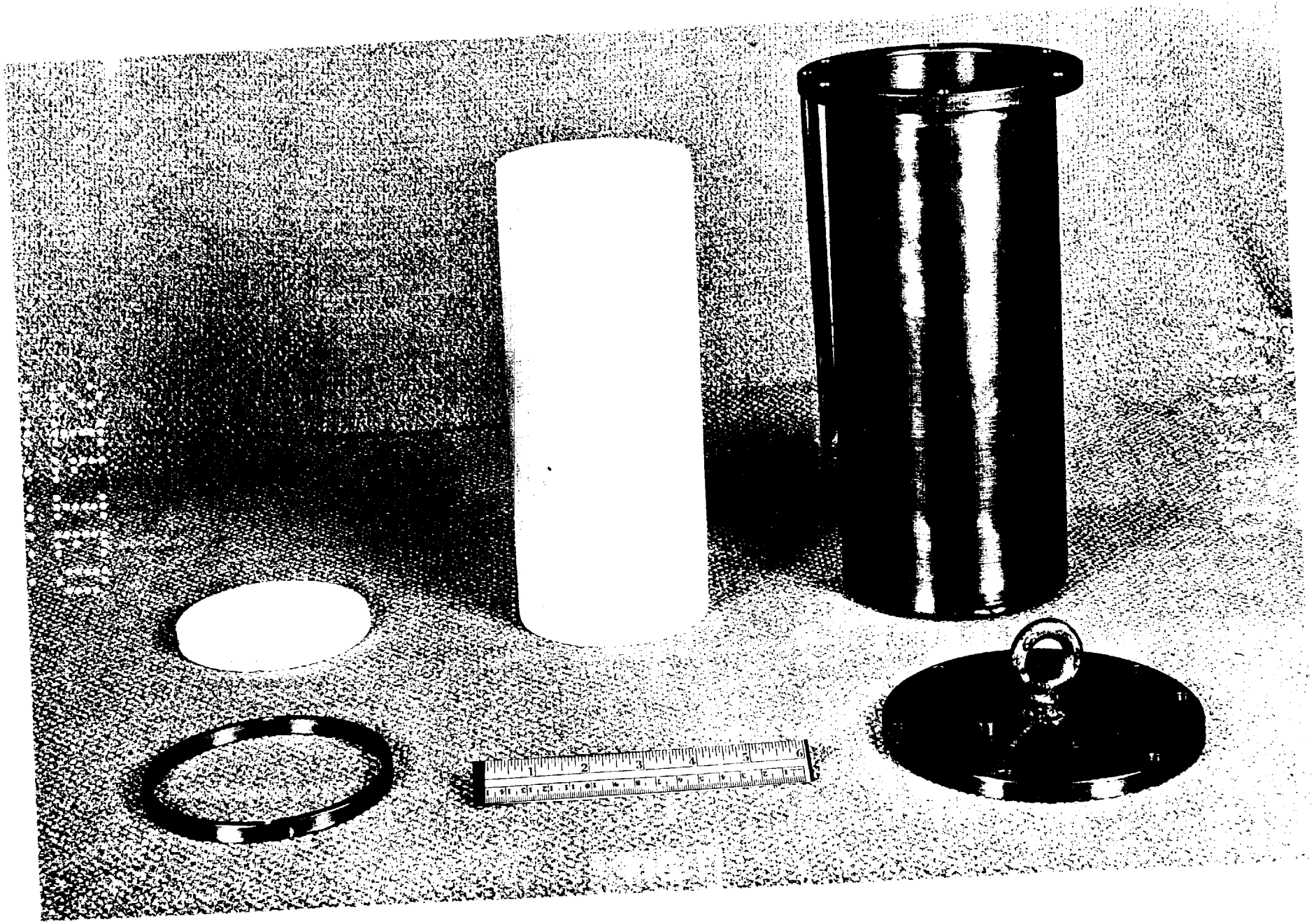
III. Reduction Results:

The reduction technique reported here gave an average yield of 99.86 o/o, an unusually high figure for reduction efficiency of any metal. Each metal button was sampled for spectrographic analysis. A summary of the analyses is given in Table IV. Values are given in ppm.

TABLE IV

Element	Max.	Min.	Ave.
La	< 0.2 ppm	< 0.2 ppm	< 0.2 ppm
Be	< 0.05	< 0.05	< 0.05
B	1.1	0.05	0.22
Na	< 5	< 5	< 5
Mg	50	5	12
Al	< 5	< 5	< 5
Si	350	20	58
Ca	40	< 20	

Fig. 4 is a photograph of the top and bottom of a typical metal button as delivered for machining and sectioning.



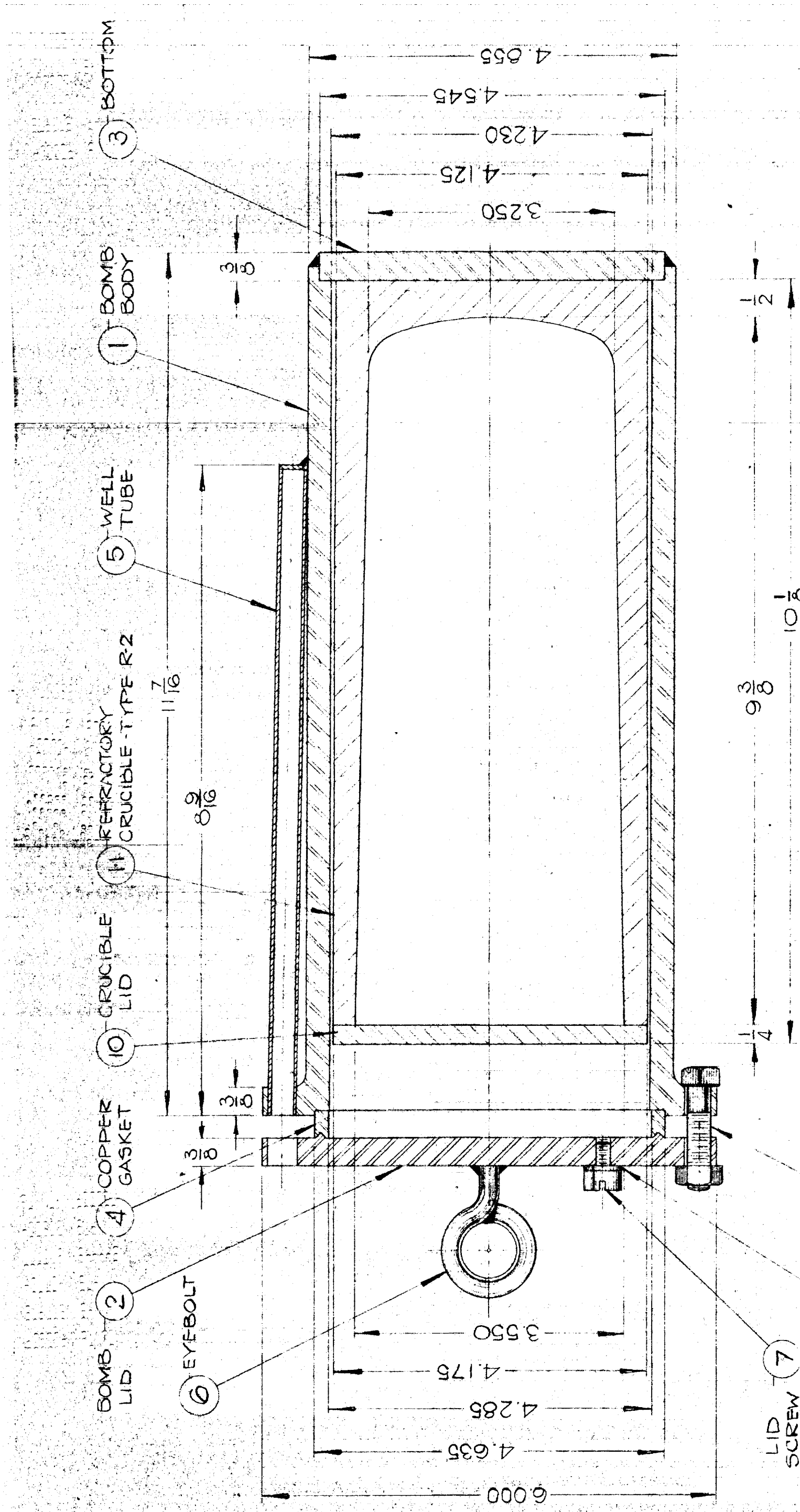


Fig. 2

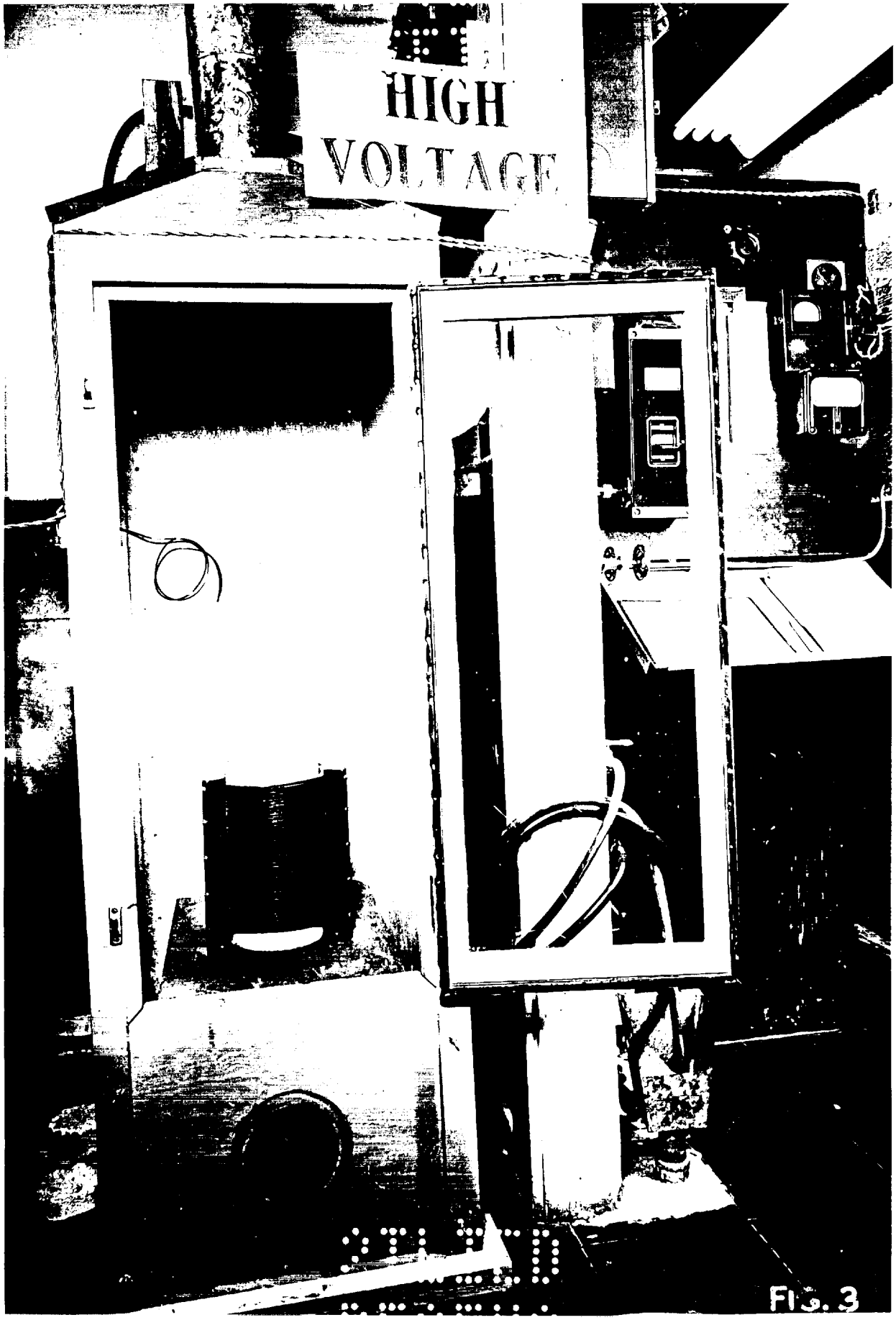


Fig. 3

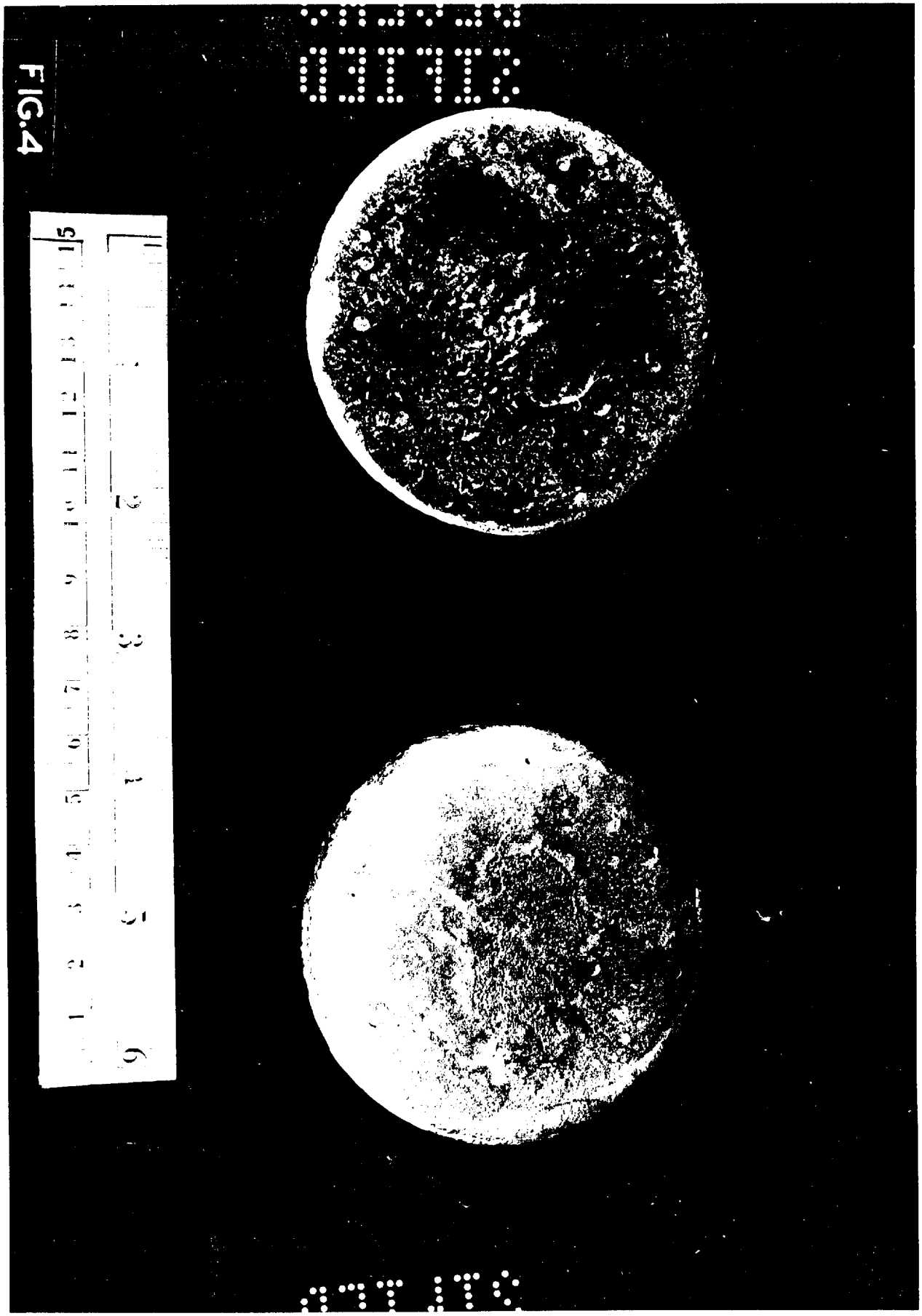


FIG.4

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