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GROWTH OF UO_2 SINGLE CRYSTALS

by

S. AMELINCKX, J. BRESSERS, K. NEVELSTEEN, E. SMETS
and W. VAN LIERDE (CEN)

1963



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Crystals from 4 to 12 mm in size, and up to 5 g in weight are easily obtained.

Control by Laue diffraction patterns and chemical analysis showed these crystals to be of high perfection and purity.

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GROWTH OF UO_2 SINGLE CRYSTALS

1. GROWTH OF UO_2 SINGLE CRYSTALS BY SUBLIMATION

1.1. Introduction

The purpose of the program, the final results of which are given, was to carry out various physical measurements on UO_2 single crystals. The single crystals grown by other experimenters are of too small dimensions for electrical, optical and thermal measurements [1]. Our aim was to grow UO_2 single crystals of at least 10 mm diameter.

By the method of electrolysis only small size crystals could be grown, and the presence of free uranium is almost unavoidable when applying methods in which UO_2 is molten [2]; we therefore tried to develop a method by sublimation.

According to the literature [3] and proved by a few orientation experiments, only a closed system could be successful.

In the mean time we found that single crystals of convenient size could be grown from the vapour phase only by very slight oversaturation. In order to realize this condition and still maintain a sufficient speed of deposition, very high temperatures were necessary, as well as very slightly cooled condensation areas and a relatively high pressure of UO_2 vapour. In case of an open system the UO_2 will be deposited on the unavoidable cold parts of the oven and the above-mentioned conditions can therefore be fulfilled only in a closed system.

1.2. Apparatus

Our apparatus essentially consists of a vacuum furnace containing two water-cooled electrodes pointing towards each other. Inbetween these electrodes fits a cylinder of pressed and sintered UO_2 which will be heated in a further described manner.

Fig. 1 displays more details of the furnace and the electrodes. A flexible connection joins one electrode ③ to the oven. Since a vacuum is created inside the oven, the outside atmospheric pressure moves this electrode towards the other one, and hereby realizes a good electrical contact between the electrodes and the UO_2 cylinder whatever may be its deformation during heating. The electrode ⑨ is fixed.

Fig. 2 gives the set-up at the electrodes extremities. Each electrode has a clamp which holds a ZrO_2 disc surrounded by a Ta foil. The ZrO_2 disc thermally isolates the electrode from the UO_2 cylinder. The Ta foil shortcircuits the electrical resistance of the refractory disc.

Together with the tantalum foil a tungsten foil is clamped joining both electrodes along the UO_2 cylinder. This tungsten foil will initially conduct the electric current and in this manner heat the UO_2 cylinder. Both open ends of the cylinder rest on a tungsten sheet which will be the condensation area.

The complete set-up of the oven is connected to a classic pumping system consisting of an oil diffusion pump and a mechanical backing pump.

The electric current supply consists of a low tension transformer fed by a variable autotransformer. A voltage of 0-15 V at a current of 300 A will feed the oven. Auxiliary apparatus for measuring the vacuum, the voltage, and the current are normally adapted.

A comparator was also positioned between the moving electrode and the oven in order to follow the displacement of the electrode and the deformation of the cylinder.

1.3. Method and results

1.3.1. Fabrication of the cylinder

The finished UO_2 cylinders are in the form and dimensions as indicated in Fig. 3.

No extrusion press being available these cylinders are pressed under a hydrostatic pressure of 5 tons/cm² in a rubber tube around a NaCl rod manufactured by pouring molten NaCl in a graphite mold.

After the pressing, the NaCl is washed by water, the cylinder is formed and dried and then sintered during 1 hour under hydrogen at 1400°C. The obtained sintering results in a density of less than 90 % of the theoretical density, rendering the cylinder less sensible to thermal shocks.

1.3.2. Sublimation

The UO_2 cylinder is inserted into the oven in the already described manner: it is clamped between the extremities of the water-cooled electrodes, and a vacuum of $\pm 6 \times 10^{-4}$ mm Hg is created. The current then passes through the tungsten foil under the cylinder. By gradually increasing the current the cylinder reaches 1000°C after 2 hours. According to Table I the electrical resistance of UO_2 as a function of the temperature is 5 Ω /cm at 1000°C [4]; the conductivity at this temperature is thus sufficient to enable heating by direct passage of current. The tungsten foil is therefore melted by a short increase of the current.

At this moment the temperature of the cylinder increases very fast to $\pm 1550^{\circ}\text{C}$ as measured on the outer wall by an optical pyrometer. An important temperature difference between outer and inner wall of the cylinder will evidently be originated. Since the outer wall cools more rapidly by radiation than the inner wall, the temperature and thus the electrical conductivity of the inner wall will soon be superior to those of the outer wall. This causes an increased current flow through the inner wall and a decreased flow through the outer wall. Owing to this semiconductor effect, the inner temperature can reach 2300°C while the outer temperature amounts to 1800°C only at the end of the preparation, thus maintaining the mechanical stability of the cylinder. The cylinder now fulfils its double function :

a) The function of container of the UO_2 vapour : as listed in Table II one obtains a p_{UO_2} of $\pm 3 \text{ mmHg}$ at 2300°C . The UO_2 of the inner wall very rapidly vaporizes and is deposited on the tungsten sheet which is slightly cooled by its supporting thermal insulator. Since great amounts of heat have to be evacuated through this sheet, its temperature is at most 100°C below that of the inner wall of the cylinder. The cylinder extremities, where the wall is conically thinned, evaporate first as proved by the shortening of the cylinder soon after the start .

After a few minutes enough UO_2 is condensated to make the cylinder vacuum tight. Since the wall itself is vapour tight, the vacuum of the furnace is maintained ; even when a thermal fissure occurs, this will be closed in less than a minute by the deposited UO_2 . Almost no UO_2 evaporates from the outer wall due to the low temperature .

b) The function of heating element : in our case some 200 A at $\pm 10 \text{ V}$ passes through the cylinder under normal conditions. This electrical resistance is ideal to generate the desired thermal effect .

In this situation we have a micro-oven consisting completely of UO_2 , wherein a relatively high pressure of UO_2 vapour is built up. Contamination is almost impossible and no technological difficulties were encountered to reach the temperature wanted .

Towards the end of the preparation the cylinder walls become rather thin . At that moment a more rapid deformation of the cylinder under the electrode pressure announces the end of the process. The electrical resistance also decreases due to the thinning of the wall. The desired current (200 A) can then only be reached by a higher voltage (15 V) and an arc might form inside the UO_2 vapour filled cylinder. The process should be shut off at this moment.

1.3.3. Results

After cooling, the cylinder and the deposits are extracted as a whole . The cylinder wall is completely recrystallized and the inner wall is covered with

very regular tetrahedrons of 0.1 to 0.5 mm. On the conical ends of the original cylinder one finds hemispherical deposits with their flat side against the tungsten sheet and their spherical surface towards the interior. These deposits weigh some 20 to 30 grams and are composed of a few crystals ; very seldom they are but one crystal .

A slight hit separates the crystals into individual single crystals . The crystal boundaries might, however, be so tight that the crystals can only be separated by sawing and cutting .

The grown crystals are up to 15 mm long and weigh up to 7 g. The total weight of the crystals, longer than 4 mm obtained from a cylinder of 100 g, amounts to 5-8 g .

1.4. Discussion

1.4.1. Method and arrangement

The arrangement described has some disadvantages which have to be eliminated. The preheating by means of a foil under the cylinder causes irregular heating which sometimes leads to fissures. In a new arrangement (see Fig. 4) the preheating is carried out by means of a tungsten spiral fed separately .

Another disadvantage of the given method lies in the fact that the deposits cool very suddenly at the end of the process. The preheating spiral is not molten and can thus be used for after-heating. The thermal contact between the electrodes and the deposits will also be disrupted. The moving electrode therefore slides some 15 mm backwards allowing the pins ④ by the action of the springs ③, to move the ZrO_2 disc, with the deposit a few mm away from the extremities of the electrodes. These arrangements permit a controlled cooling .

Due to the negative temperature coefficient of UO_2 the cylinder heated by direct current passage, constitutes a very divergent electrical system which is therefore difficult to stabilize. In the new arrangement the manual control was replaced by an automatic stabilization, the current being stabilized by a dry thyatron .

1.4.2. Growth mechanism

1.4.2.1. Structure of the deposit

We now consider the obtained sublimates in more detail. Fig. 5 represents a sublimate as obtained. The growth surface is very shiny and the grain boundaries are clearly marked. During the early phase of this investigation surface features were observed whose origin was not immediately understood [5]. Chemical analysis showed a rather important impurity content of tantalum. By condensing on a tungsten sheet the contamination as well as the associated features disappeared .

The flat surface of the deposit, lying against the condensation sheet, is a polycrystalline layer. On this layer one finds an area of columnar crystals developing towards the growth surface. The thickness of this area is at most one mm in the central part of the sub-layer and up to 5 mm at the edges. Some of the columnar crystals grow and become the large crystals of the deposit. They usually have a very small base and grow larger towards the growth surface.

1.4.2.2. Mechanism

All deposits have their $\langle 111 \rangle$ direction perpendicular to the base, the maximum deviation being a few degrees. Large crystals often show the development of a small $\langle 111 \rangle$ facet observed as a circle on the spherical growth surface. Obviously, the large crystals grow according to a double mechanism :

- (a) A polycrystalline layer is first deposited on the cold condensation sheet ; with increasing temperature it acquires a certain orientation resulting in growth of columnar crystals. Only a few of these crystals will develop, in particular these whose slowest growth direction is perpendicular to the condensation area, hampering the development of the other crystals by their lateral growth.
- (b) The other mechanism is the growth by grain boundary migration. The form of the deposits proves that the temperature at the central part of the deposits is lower than at the edges. Indeed, the contact resistance of the cylinder walls causes a strong local heating on the condensation sheet. Due to this effect, a radial thermal gradient exists in the deposit and the grain boundaries will migrate under the influence of the thermal stresses. Two supplementary observations confirm this : Fig. 6 shows a grain boundary ; the original position of the grain boundary, which has migrated, is clearly visible. Another indication was found during the attempts to prepare crystals doped with a controlled amount of Al_2O_3 and Nb_2O_5 . Before pressing some 500 ppm of these oxides were added to the UO_2 powder.

These experiments proved that it is impossible to grow large crystals by this method. Some crystals of more than 4 mm were obtained but they had no more than 150 ppm impurity content. The impurities evidently segregate towards the grain boundaries and prevent their migration. By hindering the migration of the grain boundaries the development of the crystals is limited to slightly enlarged columns with a maximum diameter of 4 mm.

1.4.2.3. Chemical purity

Chemical analysis proved that almost no impurities are introduced during the process. In Table III the spectrographic analysis of the starting material is compared with this of the obtained crystal. Considering the less accurate results of the analysis, we conclude that no impurities are introduced. A special analysis showed 16 ppm of W in individual crystals ; the polycrystalline layer contained 350 ppm of W.

The O/U ratio has been determined by means of polarographic measurements of U^{VI} in a phosphoric acid medium ; by developing this method up to the extreme limits of accuracy, the O/U ratio was found to be 2.0001. As for the stoichiometric composition no discrepancy could be found by lattice parameter measurement.

1.4.2.4. Physical perfection

Laue diffractograms proved that the crystals have no misorientation as shown in the reflection image of Fig. 7. Electron microscopy proved that large areas exist without dislocations in spite of the fact that at the end of the process the crystals were quenched by a temperature drop from 2300°C to 1000°C in plus minus one minute. In order to obtain starting material for the study of dislocations, the crystals have to be deformed mechanically.

It was also possible to cleave the crystals, principally along the [111] plane but also along the [110] plane.

1.5. Conclusion

The given method which can undoubtedly be applied for the preparation of single crystals of other materials than UO_2 , has proved to be reproducible, unexpensive and simple ; single crystals of excellent chemical and physical qualities of more than 10 mm size can be obtained which are suited for almost all physical measurements on UO_2 .

Table I

°C	Ω / cm
100	400
200	100
300	60
400	25
500	18
600	12
700	10
800	8
900	6
1000	5

Table II

°C	P_{mmHg}
1351	$1.55 \cdot 10^{-3}$
1504	$7.07 \cdot 10^{-7}$
1727	$6.57 \cdot 10^{-5}$
1955	$3.60 \cdot 10^{-3}$
2151	$4.21 \cdot 10^{-2}$
2388	$9.55 \cdot 10^{-1}$

Approximate electrical resistivity of sintered $UO_{2.01}$

Table III

Impurity (in ppm)	Al	Si	Fe	B	Mg	Pb	Cu	Ca	Cr	C	O/U ratio
a) starting material	10	20	12	0.2	5	-	-	5	10	50	2.07
b) crystals	12	20	9	0.17	18.5	4	5	45	10	50	2.0001 $\pm .0001$

References

- [1] R.G. ROBINS, J. Nucl. Mat. 3, 294 (1961)
- [2] R. COLOMBO, J. Nucl. Mat. 5, 259 (1962)
- [3] BMI Reports relating to civilian applications 1960, 1961, 1962
- [4] DEG Report 120 (R)
- [5] W. VAN LIERDE, R. STRUMANE, E. SMETS and S. AMELINCKX, J. Nucl. Mat. 5, 250 (1962).

2. THE PREPARATION OF UO_2 SINGLE CRYSTALS FROM A MOLTEN SALT SOLUTION OF URANYL CHLORIDE

2.1. Introduction

This report describes the studies in the preparation of uranium dioxide single crystals from molten salt solution.

It was found by HAMPE [1] in 1888 that UO_2 could be produced by electrolysis of a molten uranyl chloride solution.

GIBSON and WASSELL [2] also investigated the electro-deposition of uranium dioxide from solutions of uranyl chloride in fused alkali metal halide melts using carbon electrodes. The electrolytic UO_2 obtained was suitable either as oxide particles of the correct size for dispersion type fuels, or for consolidation by swaging techniques. The same process was studied by LYON and VOYLAND [3]. The material obtained had physical properties which make it potentially useful as a ceramic fuel material.

The pilot plant production of electrolytic uranium dioxide was also investigated by CHALKLEY [4]. The process has been found capable of producing oxides within the range of composition UO_2 to $UO_{2.5}$.

It was ROBINS [5] who first decided to use this process to obtain single crystals on the cathode surface. We considered it worth while to take up ROBINS's method in order to investigate the possibility of obtaining large UO_2 single crystals suitable for a variety of physical measurements.

It was admitted that under particular conditions of cathode current density, applied potential and temperature of operation separate single crystals can be obtained on the cathode surface.

2.2. Experimental

2.2.1. Apparatus

As in ROBINS's experiments, the electrolysis cell consists of a round bottomed vitreous silica tube 5 cm bore x 25 cm long, which contains 600 g of melt. The cell is fitted with four holes to accommodate two electrodes, a vitreous silica thermocouple pocket and an argon inlet tube (see Fig. 8).

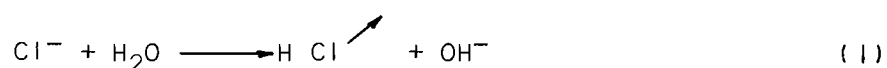
The cathode consists of a platinum sheet 2 cm x 4 cm x 0.1 mm. It is connected to a platinum wire, protected by a vitreous silica capillary. The anode is a high purity graphite rod 5 mm diameter x 30 cm long. A furnace of 1.5 kW is used to melt the salt. The temperature is measured and controlled by a Foster regulator.

The circuit used is shown in Fig. 9. A constant voltage is supplied by a storage battery, in series with a variable resistance, the cell itself and an ammeter. Direct readings are taken from this ammeter and the voltmeter connected in parallel with the cell. The applied potential, current and temperature are recorded by a Cambridge recorder.

To prevent air diffusion in the cell a slight overpressure of argon is maintained in the cell. To purify the argon, the gas flows through three tubes containing calcium chloride, silicagel and phosphorous pentoxide in order to absorb water vapour. It then flows through one tube containing an active Cu BTS catalyser of the Badische Analin & Soda Fabrik in order to absorb oxygen.

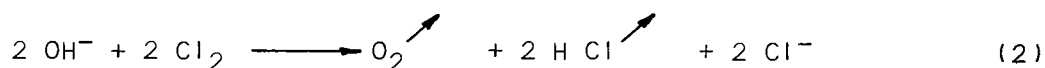
2.2.2. Melt preparation

The eutectic mixture of NaCl - KCl is chosen as solvent on account of its relatively low melting point (660°C) and its ability for drying. Indeed, if moisture is not removed, hydrolysis occurs as indicated by eq. (1).



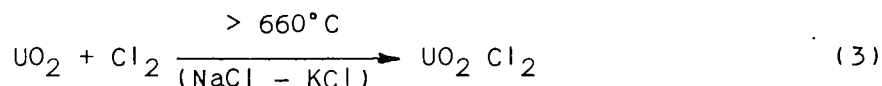
A recent method developed by MARICLE and HUME [4] can be used to remove the hydroxide impurities. This is achieved by passing chlorine through the melt as soon as the melting point of the undried salts is reached.

This reaction is presumably :



The hydroxide ion is thus removed without contaminating the melt by some extraneous non-volatile species. The oxygen and hydrogen chloride gases are swept out of the chlorine. In accordance with MARICLE and HUME the hydroxide ion concentration is lowered below a level detectable polarographically after about 30 minutes of treatment with chlorine.

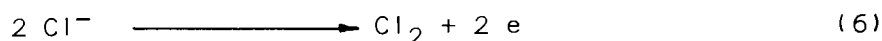
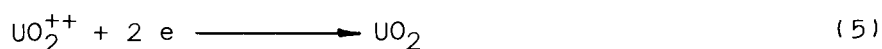
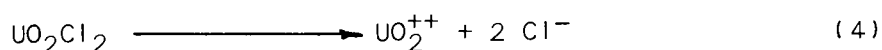
Uranyl chloride is prepared by passing chlorine through the sodium - potassium chloride melt in which UO_2 powder has been suspended. This reaction can be written as



2.2.3. Electrolytic reduction of uranyl chloride

The standard potential of UO_2^{++} (VI) - UO_2 (IV) in the LiCl - KCl eutectic has been measured at $450^\circ C$ by HILL et al. [7]. The value obtained by these authors is -0.285 ± 0.005 volt against a standard Pt(II) - Pt (0) reference electrode. This value has been taken as a rough approximation in our system.

The expected reactions are



2.2.4. Procedure

After melting the salt, chlorine is injected into the bottom of the cell through a silica tube. The temperature is increased to $840^\circ C$. After one hour of chlorination pure UO_2 powder is added to the melt. When the melt becomes reddish-orange, the uranium oxide is completely dissolved in the salt. The electrode assembly is then introduced. The electrolytic current is adjusted to 50 mA, which corresponds to a cathode current density of 4 mA/cm^2 . When the run is stopped the platinum cathode is cooled in air. The deposit is then carefully washed with dilute HCl, distilled water, acetone and ether.

2.2.5. Current density

ROBINS found that the optimum current density must be such that UO_2 crystals nucleate on the cathode surface at a mean distance of about 5 mm. This is necessary in order to avoid cross-over growth, particularly if one wants to obtain large crystals. The influence of concentration and current density are in one way complementary. By increasing the concentration a higher current density is allowed before the deposition becomes spongy.

According to GLAZUNOV [8] the increase of the concentration should result in an increase of the crystal size in the direction parallel to the cathode surface and in a decrease in the direction perpendicular to it.

2.2.6. Polishing experiments of the cathode surface

After each electrolysis experiment it has been found necessary to polish the platinum foil again. Mechanical, electrolytic and chemical methods were tried.

Electropolishing of the platinum foils was performed under the following conditions :

electrolyte : sodium chloride, potassium chloride or sodium chloride-potassium chloride eutectic composition.
 temperature : 1000°C
 current density: 15 mA/cm².

Mechanical polishing with a diamond paste gave better results and permits to use the platinum foils in more than five runs.

2.2.7. Anode material

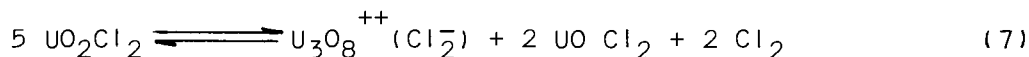
In one electrolysis we replaced the carbon anode by a sintered uranium oxide rod (6 mm diameter x 100 mm long) .

The electrolysis was carried out with the melt open to the air and with a current density of 4 mA/cm² . The deposit consisted of fine crystals of U₃O₈ .

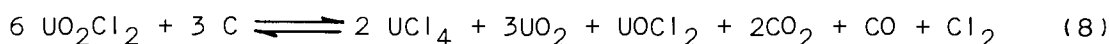
2.3. Discussion

Preliminary experiments show that it is possible to deposit UO₂ crystals below the apparent decomposition potential of UO₂⁺⁺ ions. Small crystals of UO₂ have also been deposited on the carbon anode. In one electrolysis experiment we obtained on the cathode surface columnar crystals of U₃O₈ .

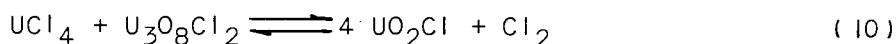
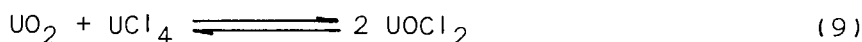
WILKS [9], who made a study of this phenomenon, suggests that two simultaneous reactions occur, namely a thermal decomposition of UO₂Cl₂ :



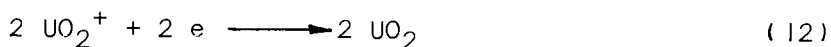
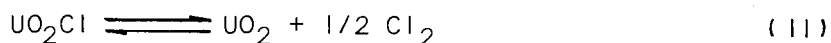
and a reaction with the carbon anode



The UCl₄ produced, reacts with the UO₂ and the U₃O₈Cl₂ as indicated by eq. (9) and (10) .



The UO₂Cl produced during these reactions is then reduced electrolytically as follows



If UCl_4 is not sufficiently formed by reaction (8), all $\text{U}_3\text{O}_8^{++}$ ions are not removed and the $\text{U}_3\text{O}_8^{++}$ ions are together with UO_2^+ ions deposited at the platinum cathode. To produce UO_2 crystals, the carbon rod is dipped 5 cm in the melt.

All experimental observations are explained by this reaction mechanism.

2.4. Conclusion

It is concluded that ROBINS's method is only suitable to obtain relatively small crystals ; the real solution to the problem of making larger single crystals seems therefore to be the sublimation method described in section 1.

The average size of UO_2 crystals obtained on the cathode was 1 mm. Fig. 10 shows a macro-photo of the deposit on the platinum cathode. Fig. 11 and 12 show the structure surface of the crystals. The runs were performed under the following conditions :

- temperature : 840°C
- applied potential : 100 - 150 mV
- cathode current density : 4 mA/cm²
- UO_2Cl_2 concentration : 15 g UO_2Cl_2 / 600 g NaCl - KCl
- electrolysis time : 20 hours
- total volume of melt : 600 g NaCl - KCl
- the majority impurities were potassium and sodium : 100 ppm.

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- 1. water inlet
- 2. water outlet
- 3. electrode
- 4. sight glass
- 5. water cooled flange

- 6. clamp
- 7. ZrO_2 slice
- 8. power leads
- 9. electrode
- 10. comparator

- 11. tombac
- 12. silica tube
- 13. UO_2 cylinder
- 14. gaskets
- 15. shield

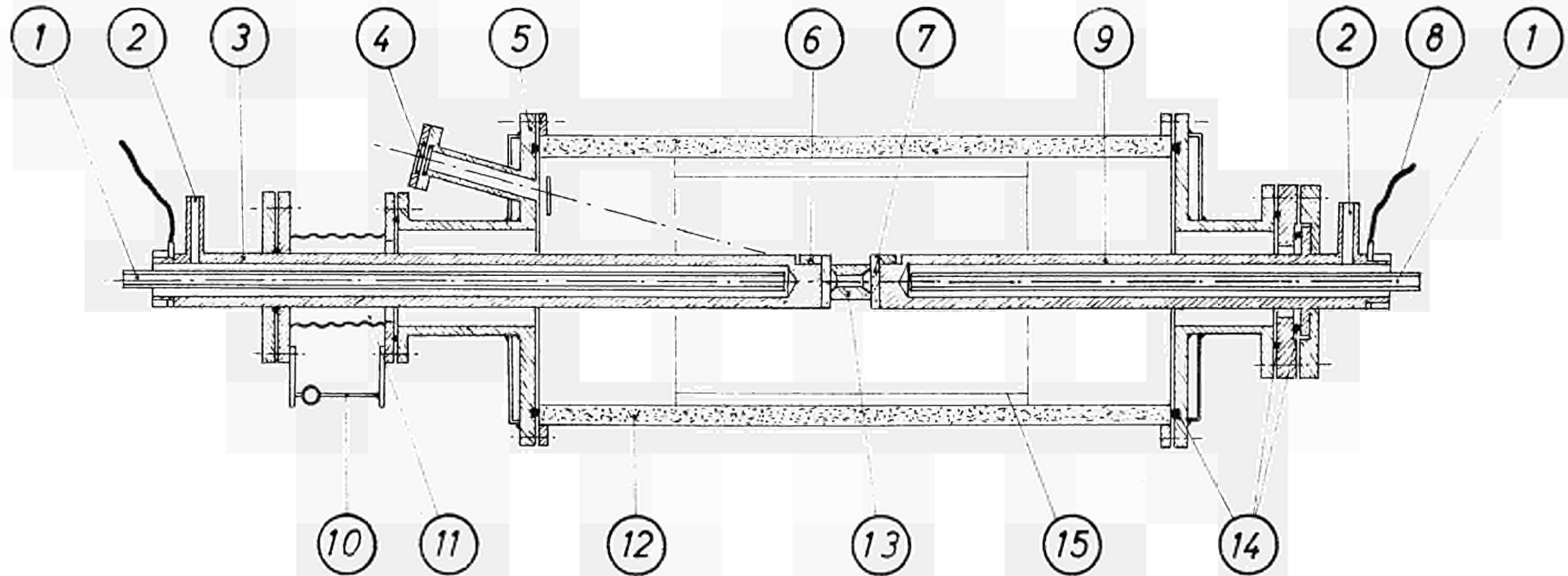
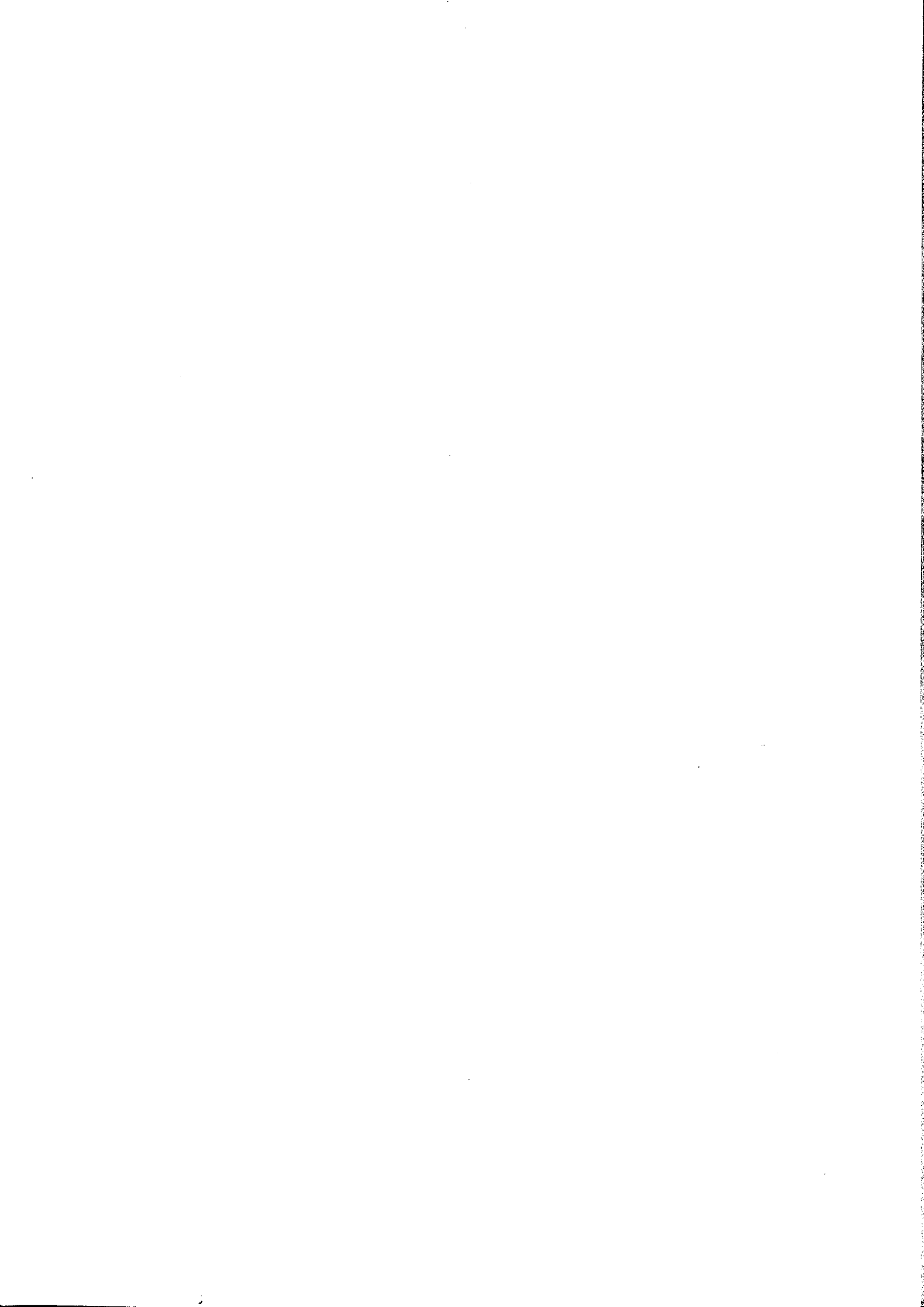


Fig. 1



1. water cooling
2. electrode
3. tungsten sheet
4. tantalum sheet

5. UO_2 cylinder
6. ZrO_2
7. clamp

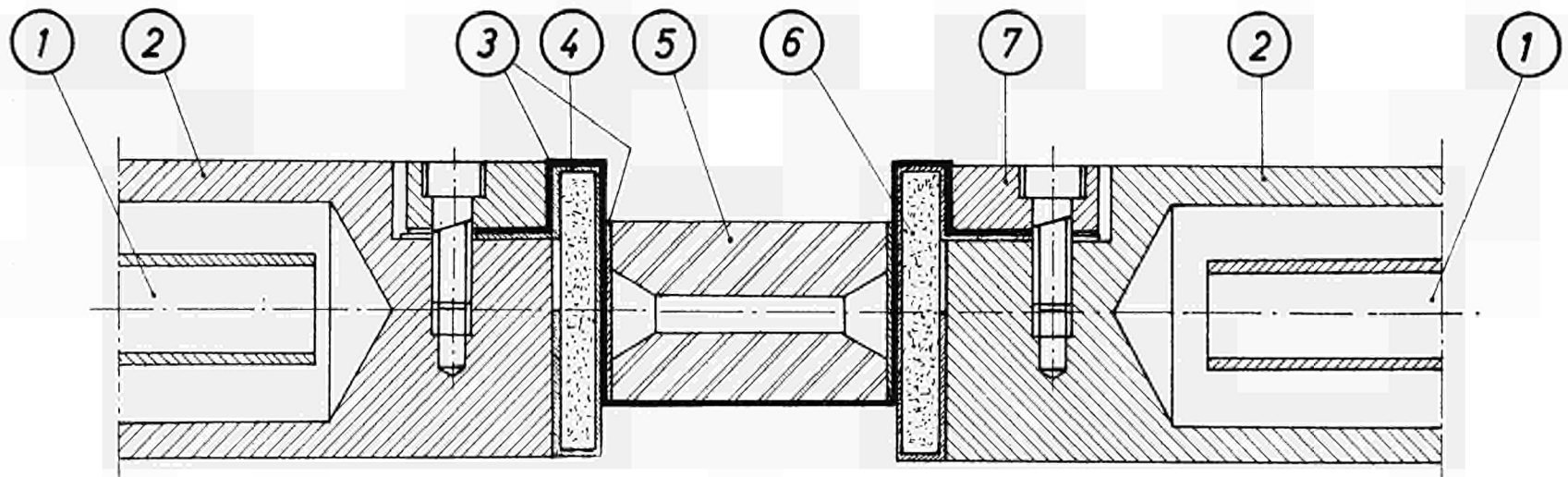


Fig. 2



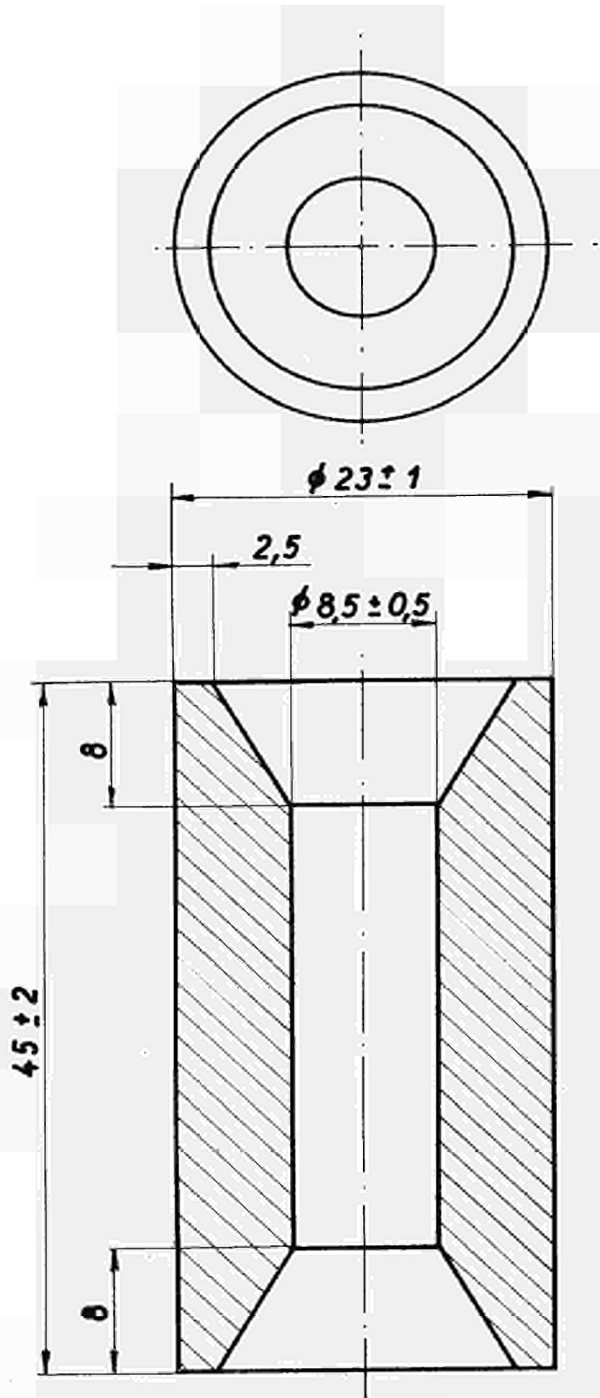


Fig. 3



1. water cooling
2. electrode
3. spring
4. pin

5. clamp
6. tantalum sheet
7. ZrO_2
8. tungsten sheet

9. UO_2 cylinder
10. wire
11. spring
12. electrode

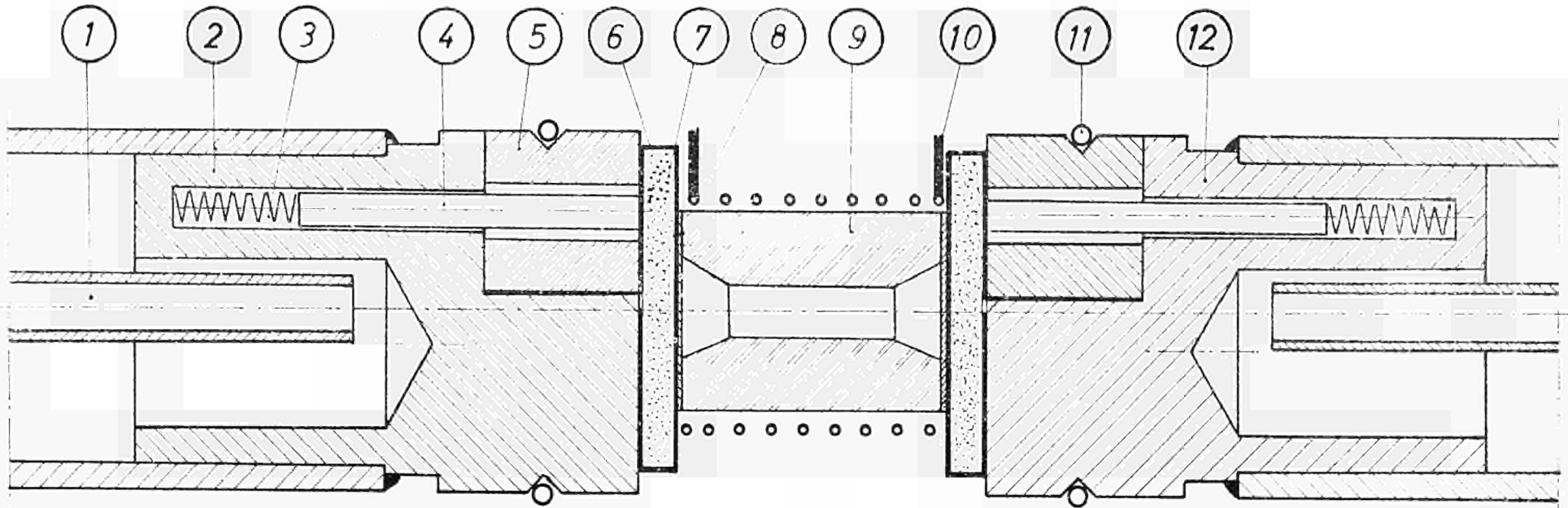


Fig. 4

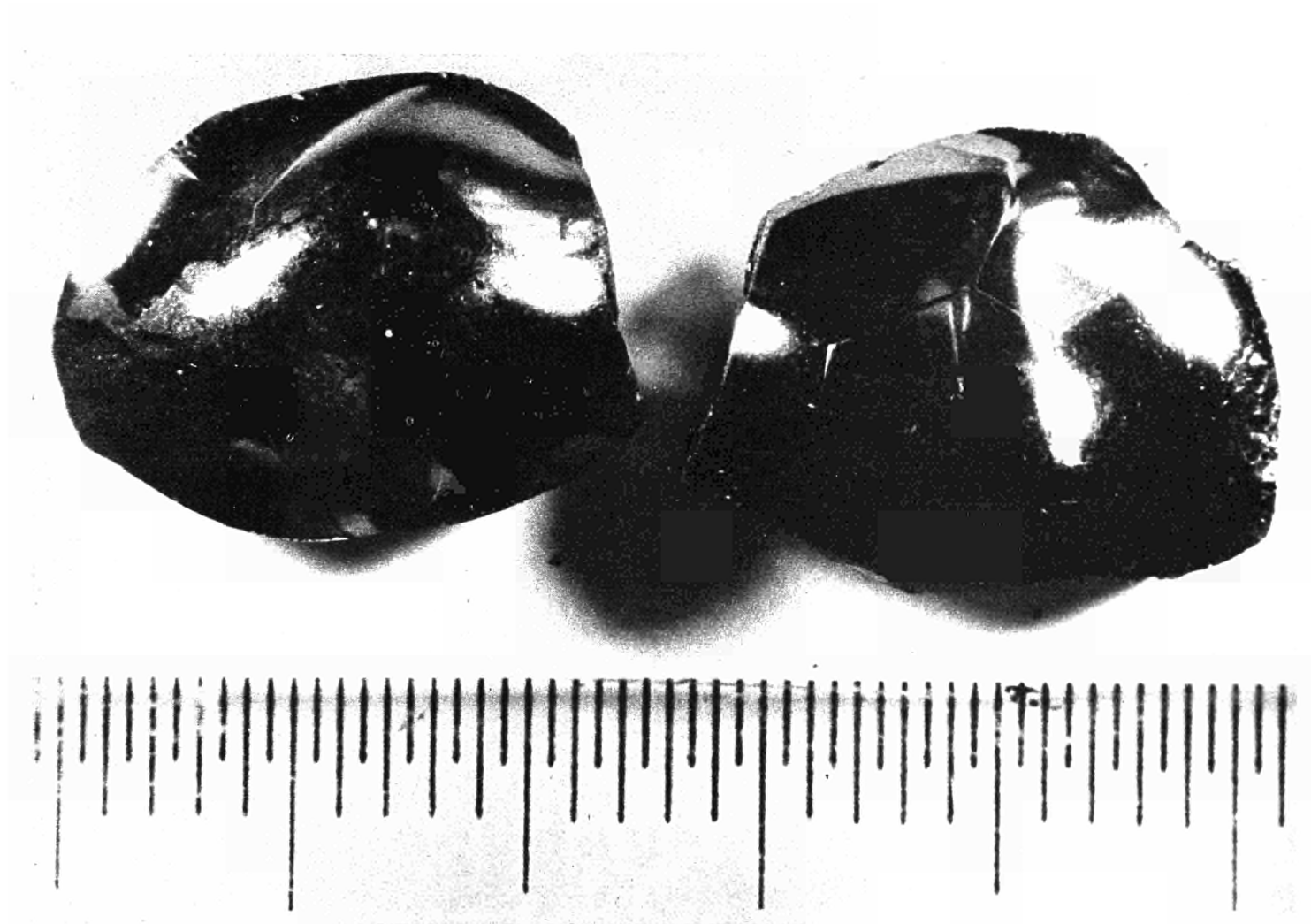


Fig. 5

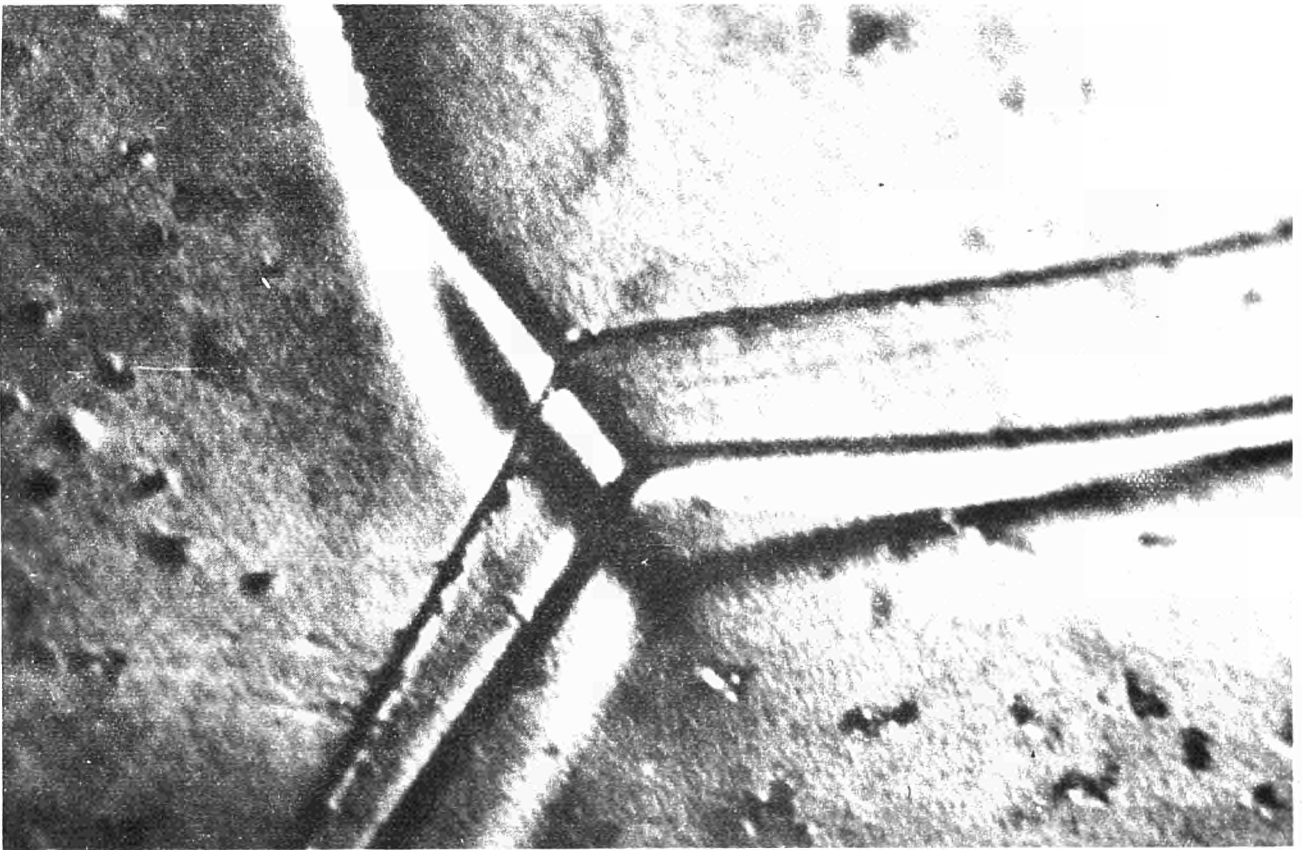


Fig. 6

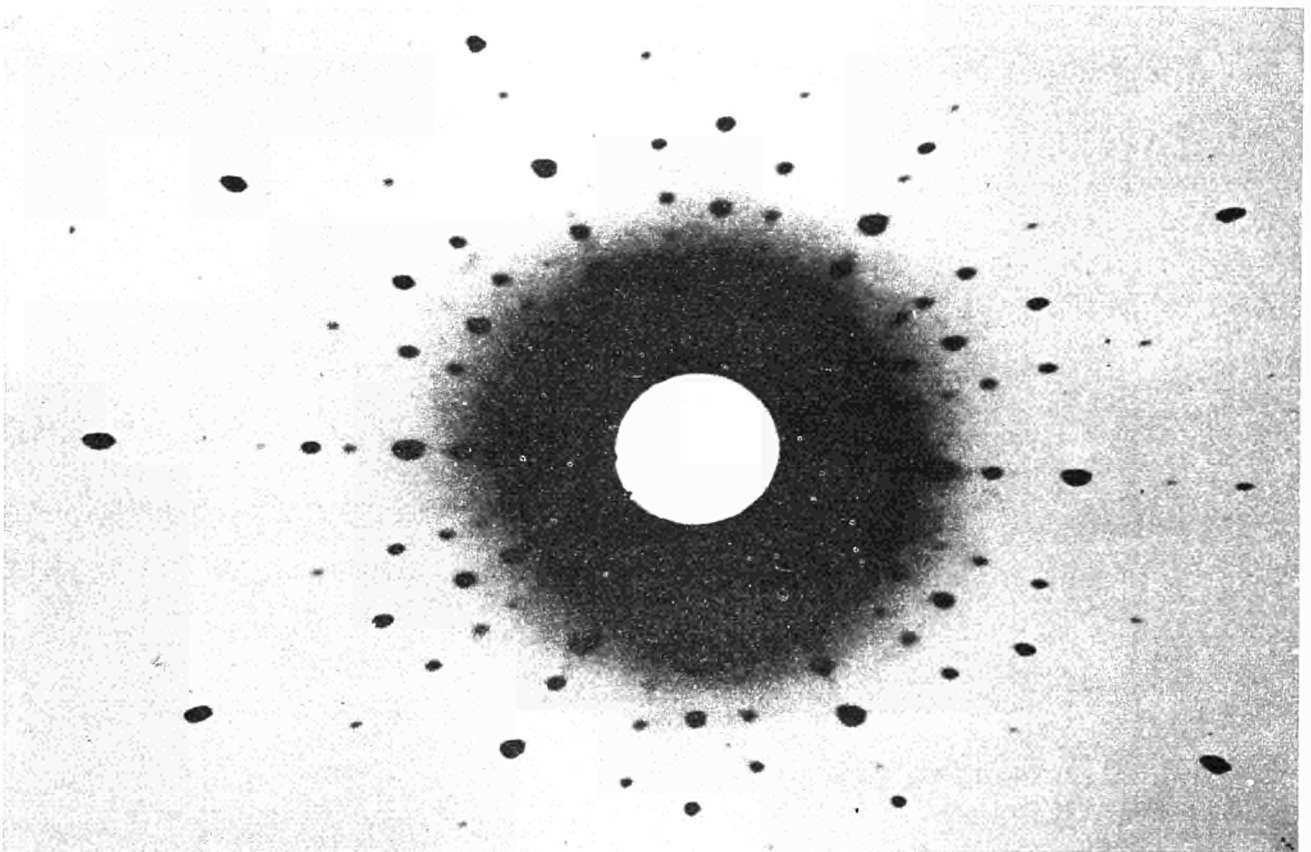


Fig. 7

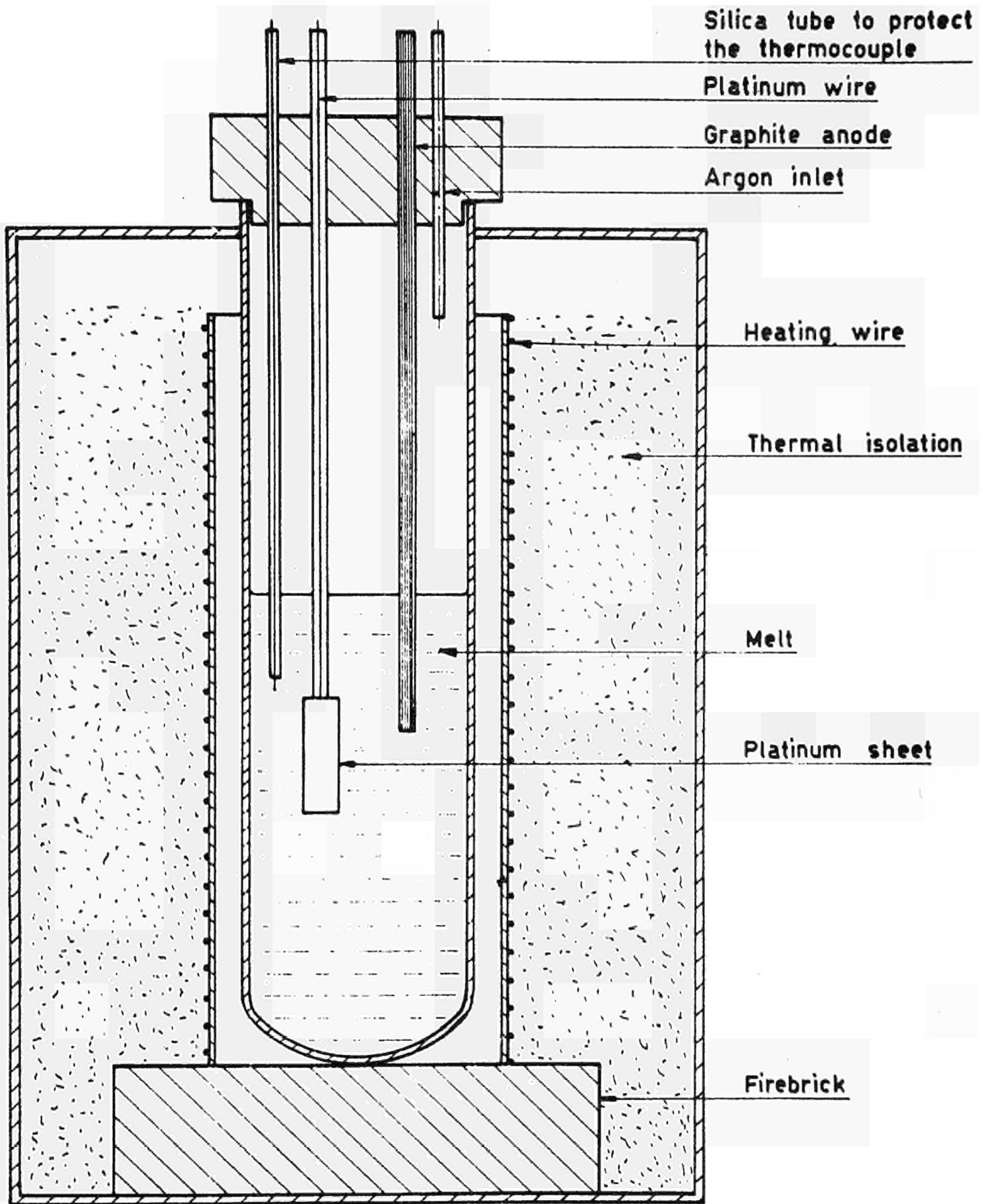


Fig. 8

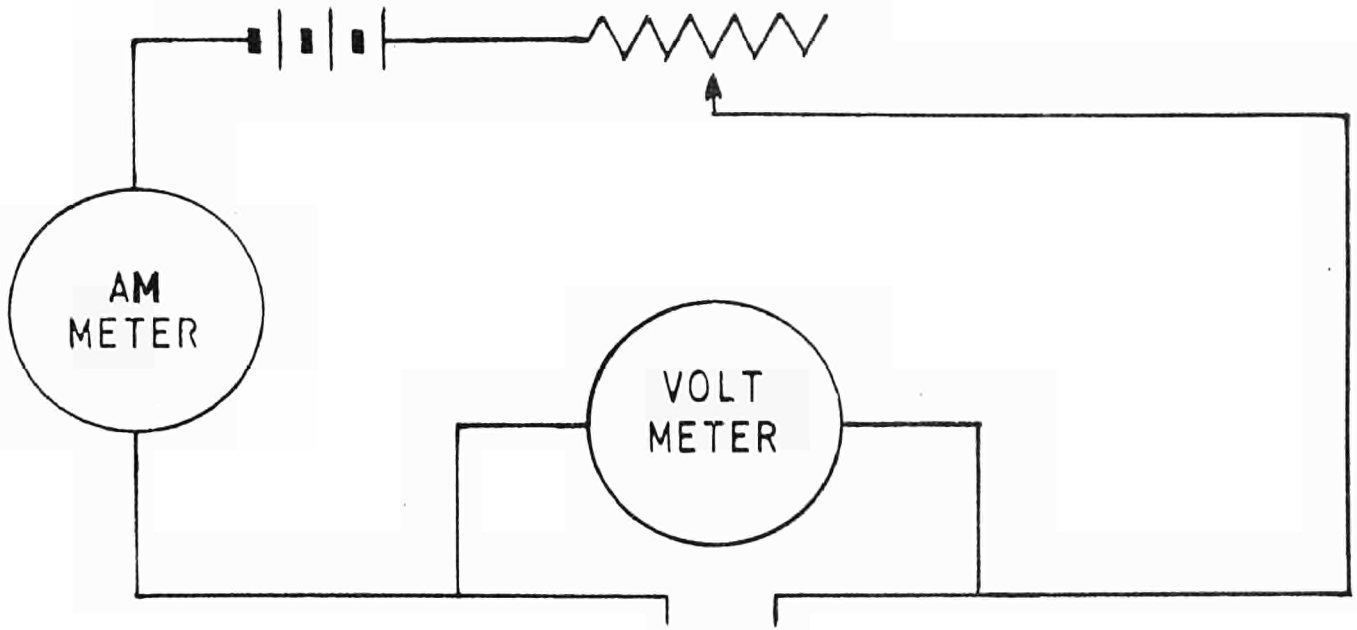


Fig. 9

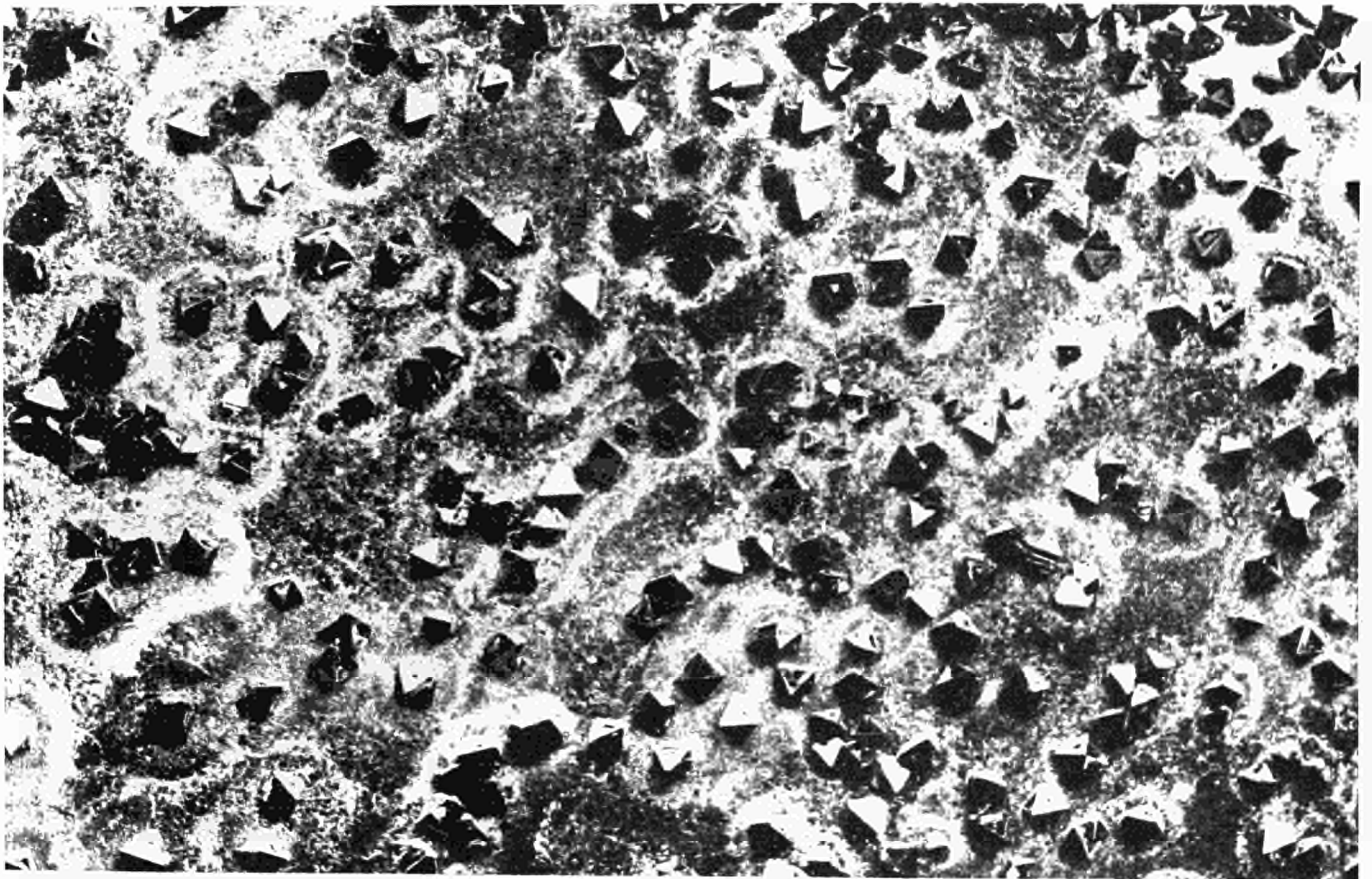


Fig. 10

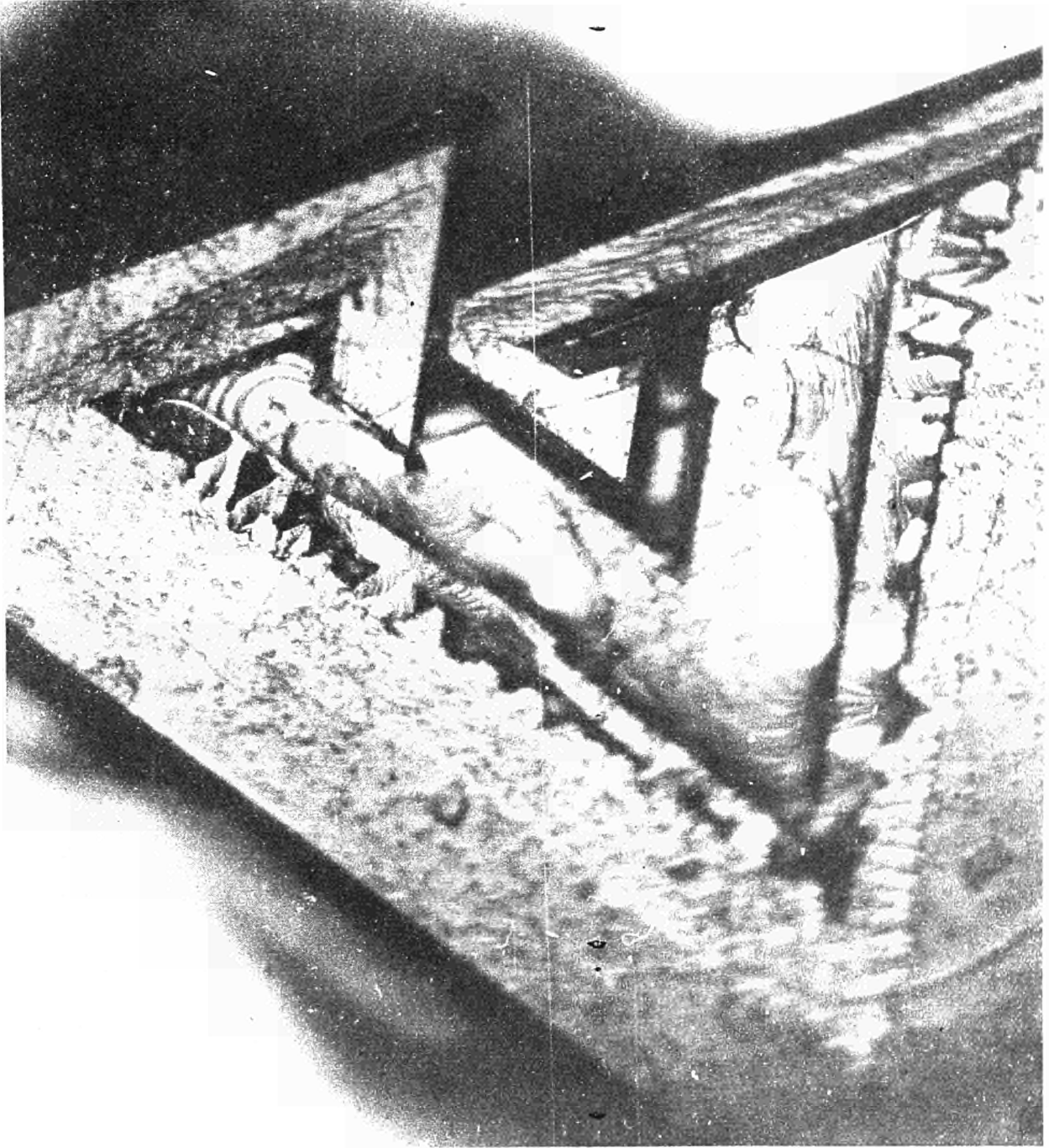


Fig. 11

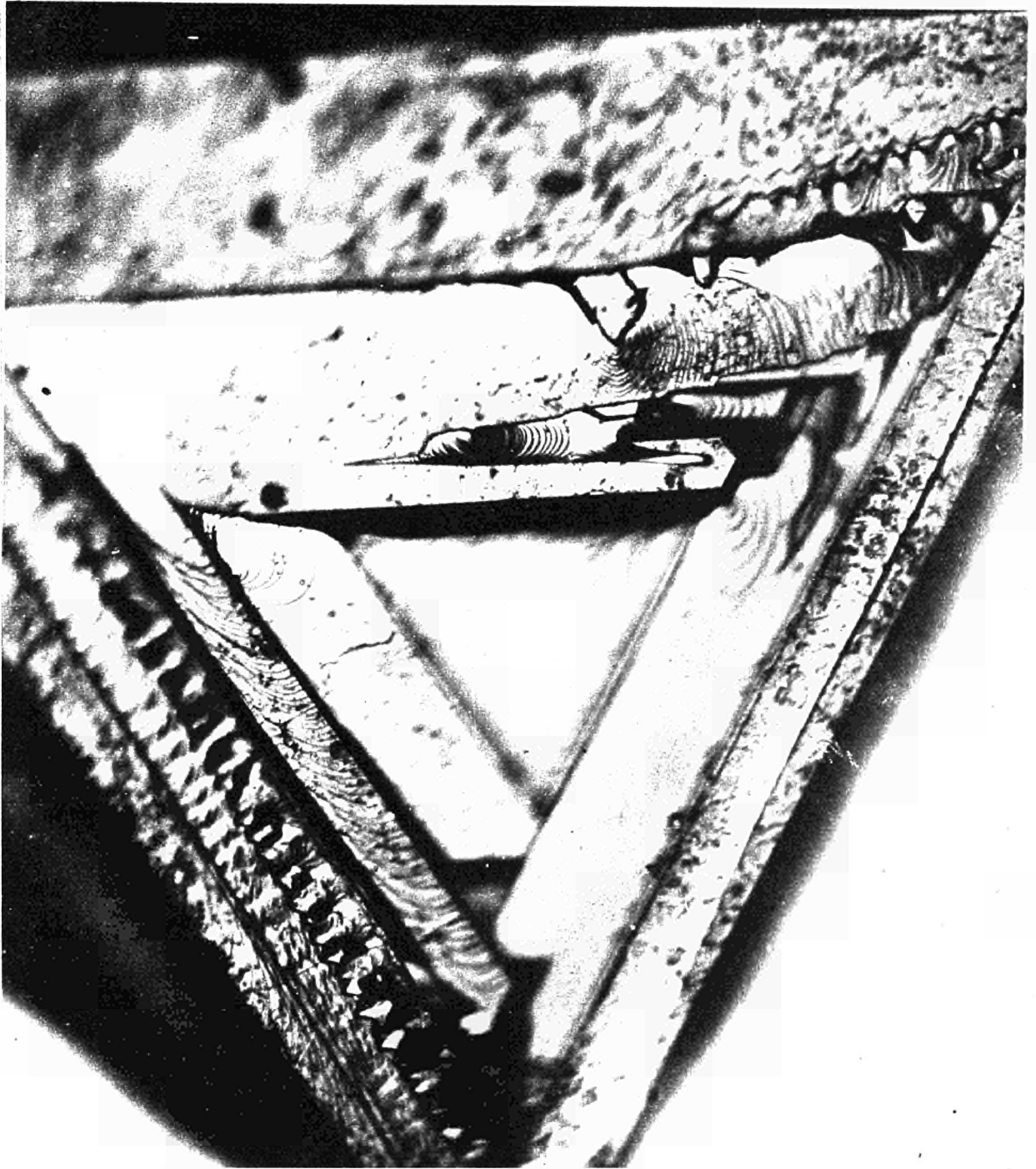


Fig. 12



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