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TO: F. L. Culler
FROM: R. E. Blanco

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1.0 INTRODUCTION

In FY 1954 work was initiated at the Oak Ridge National Laboratory on more economical methods for preparing uranium and thorium metal from their compounds. At the inception of the program criteria were established for processes which should achieve marked economy over existing methods. These were: continuous processing rather than batch; low temperature reduction; use of an inexpensive reductant; and elimination of remelting. Of the many reactions that were investigated, the reduction of uranium tetrachloride with sodium amalgam met most of these criteria and appeared most promising. The same chemistry was also found feasible for the reduction of thorium, and emphasis was shifted to this metal because of the need for increased production capacity. The process employing sodium amalgam for the reduction of uranium and thorium tetrachlorides has been named the Metallex process.

Until recently the reduction reaction was carried out between sodium amalgam and the metal chlorides which were dissolved in anhydrous propylenediamine. It has been found, however, that the reduction occurs equally well when the solid tetrachlorides are added directly to sodium amalgam. Although only a limited number of runs have been made without propylenediamine, the product appears comparable in purity and density to that obtained when propylenediamine is used. Therefore, in this discussion the Metallex process reacts solid tetrachloride with sodium amalgam directly. If it should subsequently be found that propylenediamine is necessary, the cost of thorium produced by Metallex process would not be significantly increased.

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2.0 SUMMARY

The Metallex process is a new method for producing metallic uranium and thorium. The process for producing thorium consists of the following steps (Figure 1):

1. Aqueous thorium nitrate is evaporated to molten salt and subsequently denitrated to thorium oxide.
2. Thorium oxide is reacted with carbon at 2000°C to form thorium carbide.
3. Thorium carbide is chlorinated with chlorine gas at 400°C to form thorium tetrachloride.
4. Thorium tetrachloride is reacted with 4 M sodium amalgam at 100 to 160°C to form an amalgam containing one weight per cent thorium.
5. The amalgam is washed with water and 1 M hydrochloric acid to remove sodium and sodium chloride.
6. The thorium concentration of the amalgam is increased to eight weight per cent by filtration, and to 16 weight per cent by cold pressing at 20,000 psi in a steel die to yield a solid cylinder.
7. The solid amalgam cylinders are retorted at 1100°C and < 0.1 micron pressure for one half to two hours to remove mercury. It is significant to note that massive thorium metal is produced by this process at a temperature 700°C below its melting point.
8. The sintered cylinders, in an inert atmosphere, will be compressed into a billet and extruded to form rods suitable for slug fabrication. This step of the process has not yet been demonstrated, but the measured physical properties of the Metallex product indicate its feasibility.

Typical analytical data on Metallex product show the major contaminants to be: mercury, 13-40 ppm; carbon, < 300 ppm; nitrogen, < 200 ppm; and

oxygen, ~ 2000 ppm. Cold worked Metallex thorium had a Brinell hardness of about 60. After annealing the hardness was 30.

A preliminary cost estimate was made of a 1000 ton per year Metallex plant for converting thorium nitrate to thorium metal billets. The indicated production cost was less than \$2.00 per pound of thorium including amortization. The total plant investment was \$6,980,000, and the annual operating cost was \$1,618,000. Comparative cost estimates of thorium production processes indicate that Metallex promises to be the most economical of those proposed.

3.0 PREPARATION OF THORIUM TETRACHLORIDE

Several methods for preparing thorium tetrachloride from thorium nitrate have been evaluated on a small scale. The common starting material for thorium tetrachloride is thorium oxide. Thorium oxide may be prepared by thermal decomposition of thorium nitrate or by thermal decomposition of thorium oxalate. Both of these methods for preparing thorium oxide have been well-explored and will not be considered further. The conversion of thorium oxide to thorium tetrachloride may be accomplished by several methods.

3.1 Carburization - Chlorination of Thorium Oxide

Thorium oxide may be reacted with carbon at 2000°C to form thorium carbide. This reaction is readily carried out in an electric furnace similar to that employed for the commercial production of carborundum (silicon carbide). The resultant thorium carbide reacts readily with chlorine at 400°C. The reaction rate of thorium carbide with chlorine at 400°C is approximately 30-fold greater than the rate of reaction of thorium

oxide-carbon mixtures at 500°C. Consequently, the carburization step minimizes the exposure of process equipment to the highly corrosive chlorine atmosphere. The carburization-chlorination reaction results in approximately 99% conversion of the oxide to tetrachloride. This procedure involves conventional techniques and is therefore proposed for the Metallex process. With development, however, the direct denitration-chlorination reaction which will be subsequently described promises to be superior.

3.2 Simultaneous Thorium Nitrate Denitration-Chlorination in a Flame Reactor

It has been found that thorium nitrate-carbon mixtures react rapidly with chlorine at 300-400°C. Since this method may be hazardous on a batch basis, efforts are being directed toward the development of a continuous flame reactor having only a small quantity of reactants in the reaction zone. In this case the reaction may take place in one step by the introduction of 2 M $\text{Th}(\text{NO}_3)_4$ into a hydrocarbon-oxygen-chlorine flame. Alternatively, a two-step process may be used in which 2 M $\text{Th}(\text{NO}_3)_4$ is introduced into a flame of hydrocarbon and oxygen to form thorium carbide. This mixture may be subsequently chlorinated to form thorium tetrachloride.

3.3 Direct Chlorination of Thorium Oxide

Thorium oxide-carbon mixtures may be reacted at 500°C with carbon tetrachloride-chlorine to form thorium tetrachloride. The reaction proceeds slowly, however, only about 90 per cent conversion being obtained in 4 hours. In order to obtain pure thorium tetrachloride it is necessary to sublime the products of this reaction at 800°C. This method presents many corrosion problems resulting from long contact times in chlorine atmospheres at high temperatures.

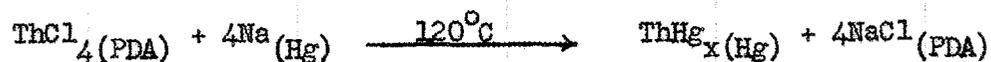
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3.4 Fused Salt Chlorination

Thorium nitrate may be denitrated by heating in a molten KCl-NaCl bath, and the resulting thorium oxide chlorinated in situ with phosgene at 680°C. The product thorium tetrachloride may be leached from the solid, pulverized salt with propylenediamine after cooling. This reaction proceeds slowly, requires large excesses of phosgene, and appears to offer no advantages for preparing Metallex feed.

4.0 REDUCTION

Most of the Metallex technology has been developed with anhydrous propylenediamine as solvent for the thorium tetrachloride which is fed to the reduction step. Thorium tetrachloride dissolves readily in hot anhydrous propylenediamine to the extent of ~ 0.5 M. The propylenediamine should contain less than 0.3% water to prevent hydrolysis and the precipitation of ThOCl₂. On contact with sodium amalgam, the thorium is reduced and transfers to the amalgam phase and sodium chloride to the propylenediamine phase,



Sodium chloride is insoluble in the organic phase and is removed by centrifugation. The clear PDA is then recycled for reuse.

Thorium has only limited solubility in mercury at 120°C and appears as a solid mercuride, ThHg_x, dispersed in the mercury phase. The thorium content of this phase is about 1 weight per cent when one volume of 4.0 M sodium amalgam is mixed with two volumes of 0.5 M thorium tetrachloride in propylenediamine. Sixty to 90% of the thorium present in the propylenediamine is reduced to the metal in a single one-half hour contact at 120°C. The ThHg_x is recovered from the amalgam phase by

filtration on a coarse fritted disc and appears as a "cheese" containing 8 weight per cent thorium. The cheese is then washed with water and 1 M HCl to remove residual sodium and propylenediamine. The amalgam filtrate is recycled to the process through an aqueous sodium hydroxide, electrolytic amalgamator where the sodium amalgam strength is restored to 4.0 M. The thorium recycle in the filtrate is less than one per cent.

Mixer-settlers may be used to obtain the contacting required in the reduction step. Other methods, such as spray columns, are also being studied on a small scale.

Recent experiments have shown that solid thorium tetrachloride reacts equally well with sodium amalgam at temperatures of 100-160°C. The products of this reaction are thorium quasi amalgam and sodium chloride. Since sodium chloride is not wet by the amalgam, it is easily removed when the amalgam is washed with water and 1 M hydrochloric acid to remove residual sodium. The product from this reaction has been found equivalent to that obtained when propylenediamine was employed as solvent for the thorium tetrachloride. Consequently, the direct reduction of solid thorium tetrachloride with sodium amalgam is proposed in the Metallex process.

5.0 METALLURGICAL TREATMENT

The conversion of thorium amalgam to billets is being studied by the Metallurgy Division at the Oak Ridge National Laboratory.

5.1 Cold Pressing

The thorium amalgam "cheese" obtained by filtration of the quasi amalgam is cold pressed at 20,000 psi, in a steel die, to a solid cylinder containing ~16 weight per cent thorium. The press acts as a filter, the ThHg_x

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remaining in the die and free mercury containing less than 1.0 per cent of the thorium passing through the die clearance. The cylinders which have been made to date measured about 1/2-1 in. dia. x 1-in. high.

5.2 Retorting

The solid amalgam cylinders are retorted at 0.1 micron pressure and 1100°C for 1/2 to 2 hours to remove mercury. During this period the cylinder shrinks to about 0.25 in. in diameter by 0.9 in. high, but retains its original geometry. Massive thorium metal with a density 80-95% that of theoretical is formed. This is an extremely important process feature in that massive metal is formed rather than a pyrophoric powder, even though the temperature employed is 700°C below the melting point of thorium. The amount of residual mercury varies with temperature and the heating time cycle employed. Heating for 1/2 hour at 1100°C reduced the mercury content to 13 ppm which is well within the tentative mercury specification of 39 ppm.* A temperature of at least 800°C has been found necessary to decompose the ThHg_x compound. Further work on the thorium-mercury system is projected. Table 1 shows typical analyses of Metallex thorium after the retorting step.

5.3 Slug Fabrication

The cylinders formed in the sintering operation will be maintained in an inert atmosphere, compressed into a billet, and the metal extruded in the normal manner. The metal is not pyrophoric but will react with traces of oxygen present in the inert atmosphere. If necessary the cylinders will therefore be cleaned with acid before extrusion to remove any oxide film.

*The specification is arrived at by comparison of the mercury slow neutron cross section with that of boron, whose permissible limit in thorium metal is 1 ppm.

$$\frac{(O_{Hg})}{(O_B)} \frac{(MW_B)}{(MW_{Hg})} = \frac{1}{39}$$

$$1 \text{ ppm B} \cong 39 \text{ ppm Hg}$$

An initial experiment on a single pellet showed that cold working was feasible, producing a plate without cracking with a Brinell hardness of < 60. After annealing, the hardness was Brinell 30. This is very soft thorium which should be excellent for extrusion purposes.

Both cold-pressed slugs and retorted cylinders have been subjected to melting at < 0.1 micron of pressure. The metal formed by this method was comparable to that obtained by retorting with the exception of the mercury content which was < 4 ppm.

Table 1

Analyses of Thorium Retorted at a Pressure of Less Than 0.1 Micron

Retorting Temperature (°C)	Total Heating Time (hr)	Density (g/cc)	Hg (ppm)	C (ppm)	O ₂ (ppm)	N (ppm)	Na (ppm)	Brinell Hardness
800	0.5	---	650	---	---	---	---	---
900	0.5	7.55	400	330	6,500	190	---	---
1050	0.5	10.25	175	110	11,500	385	---	---
1000	0.5	7.68	210	210	16,400	160	---	---
1000	2.0	11.2	---	280	2,500	---	---	30*
1100	0.5	9.40	13	1,540	2,260	104	45	---
1100	1.0	9.57	20	530	1,750	560	---	---
1100	1.0	11.1	155	520	3,400	245	---	---
1100	2.0	9.05	45	156	2,750	200	---	---

*Cold rolled and annealed.

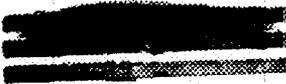
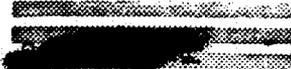


Figure 2 shows thorium metal from each Metallex processing step. Figures 3, 4, and 5 present photomicrographs of Metallex thorium. Figure 6 is a photomicrograph of typical Ames metal which has had treatment similar to that of the Metallex metal shown in Figure 4.

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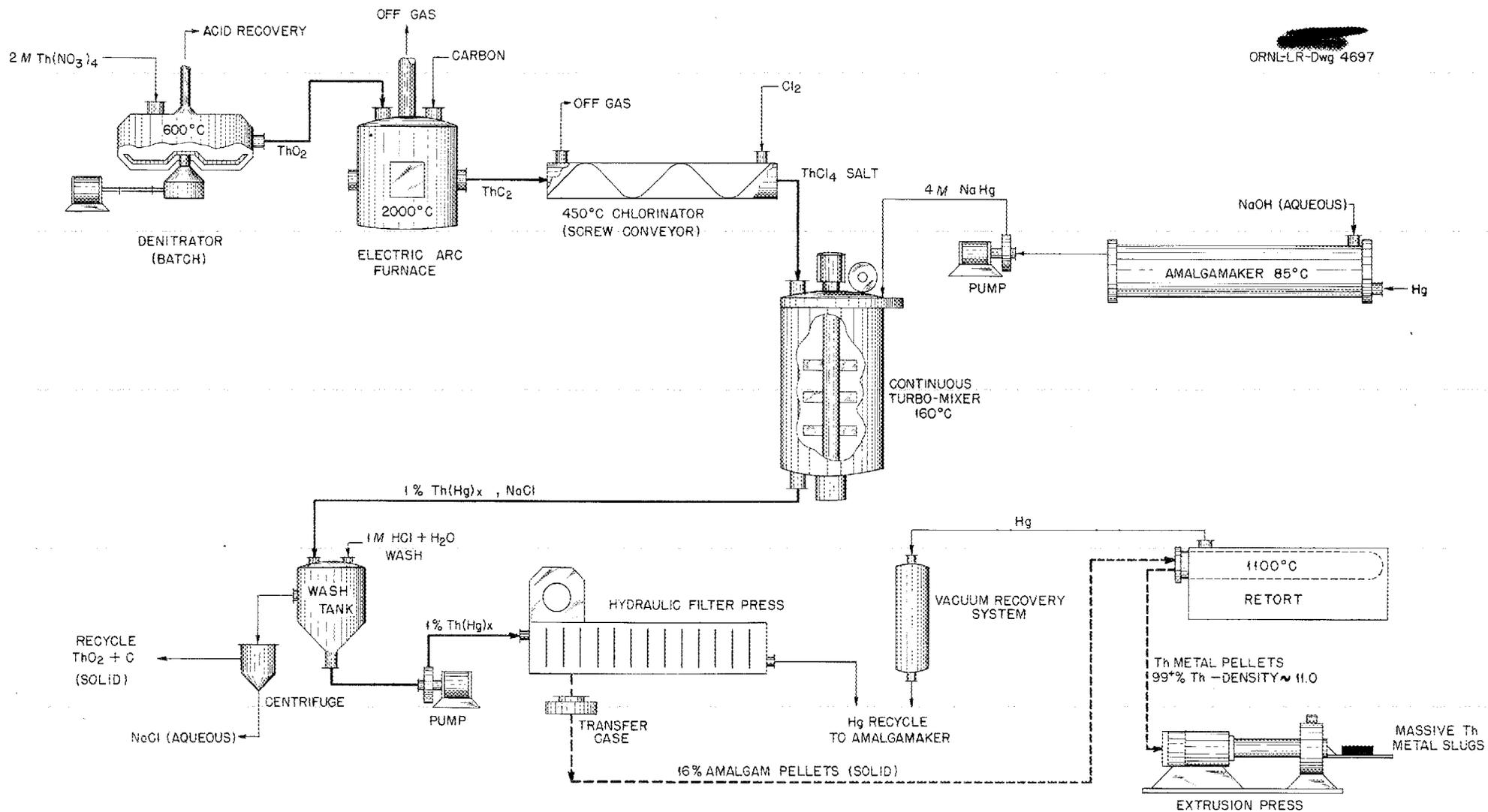


Fig. 1. METALLEX PROCESS

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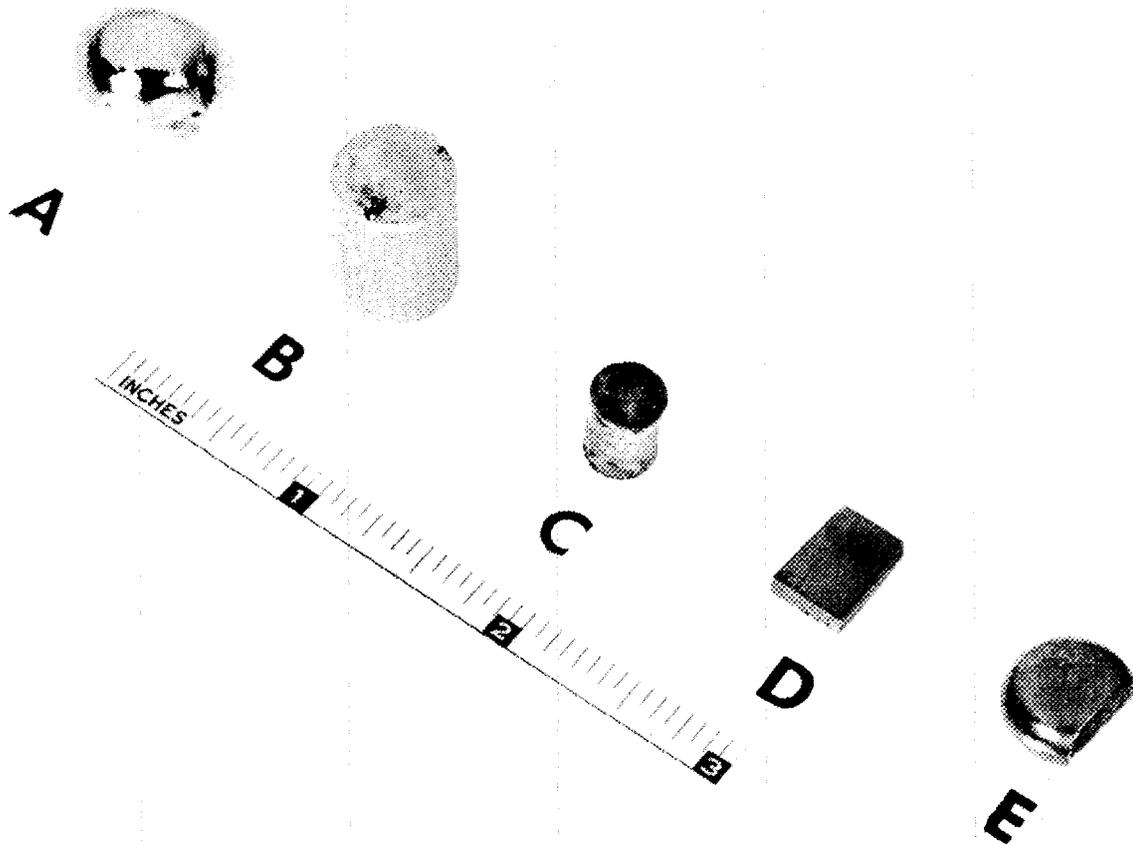


Fig. 2. Metallex Product From Various Processing Steps.

- A- Amalgam filter cake-eight weight percent thorium.
- B- Amalgam cylinder formed by cold die pressing - 16 weight percent thorium.
- C- Thorium cylinder after retorting.
- D- Sample C after cold working to 50% reduction in thickness.
- E- Sample C after arc melting.

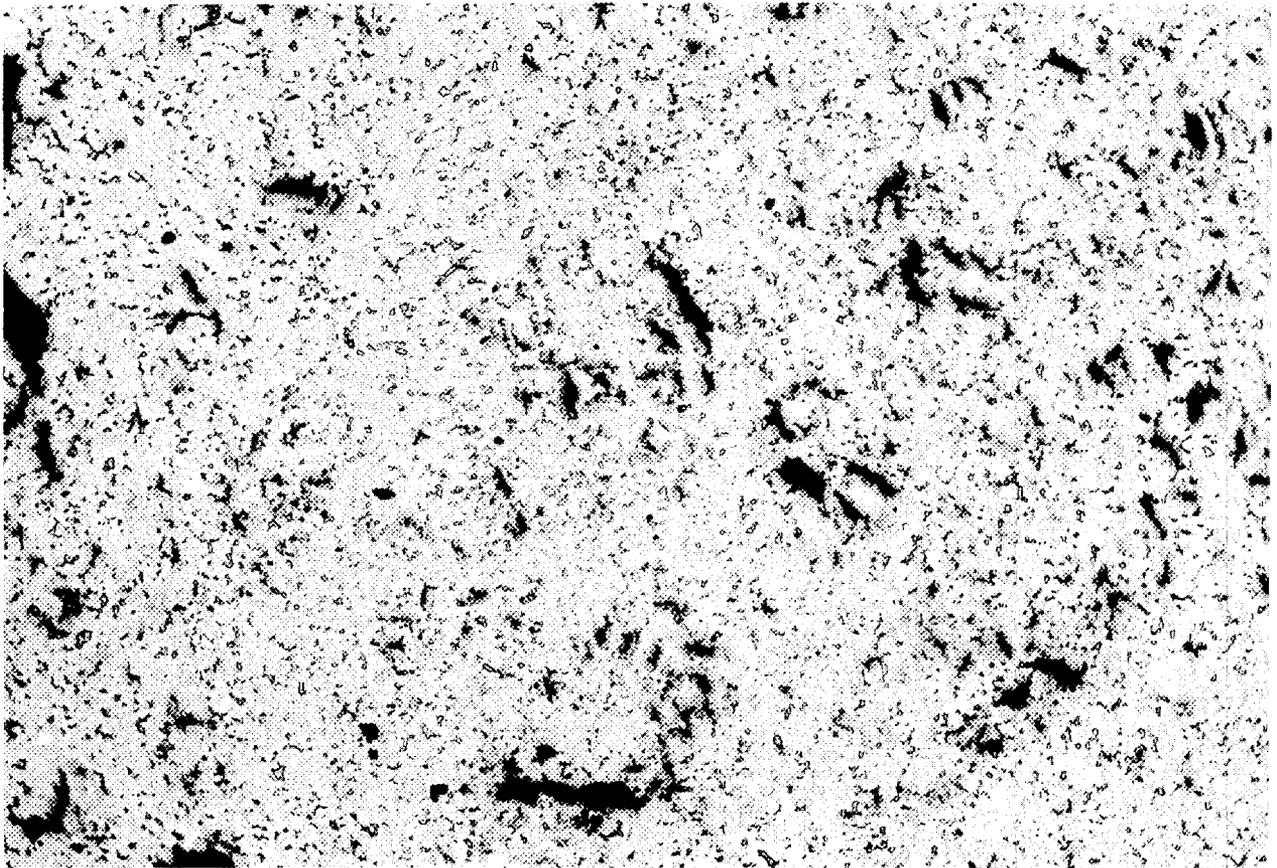


Fig. 3. Photomicrograph of Metallex Thorium Cylinder Retorted for 1/2 hour at 1000°C. 100X.

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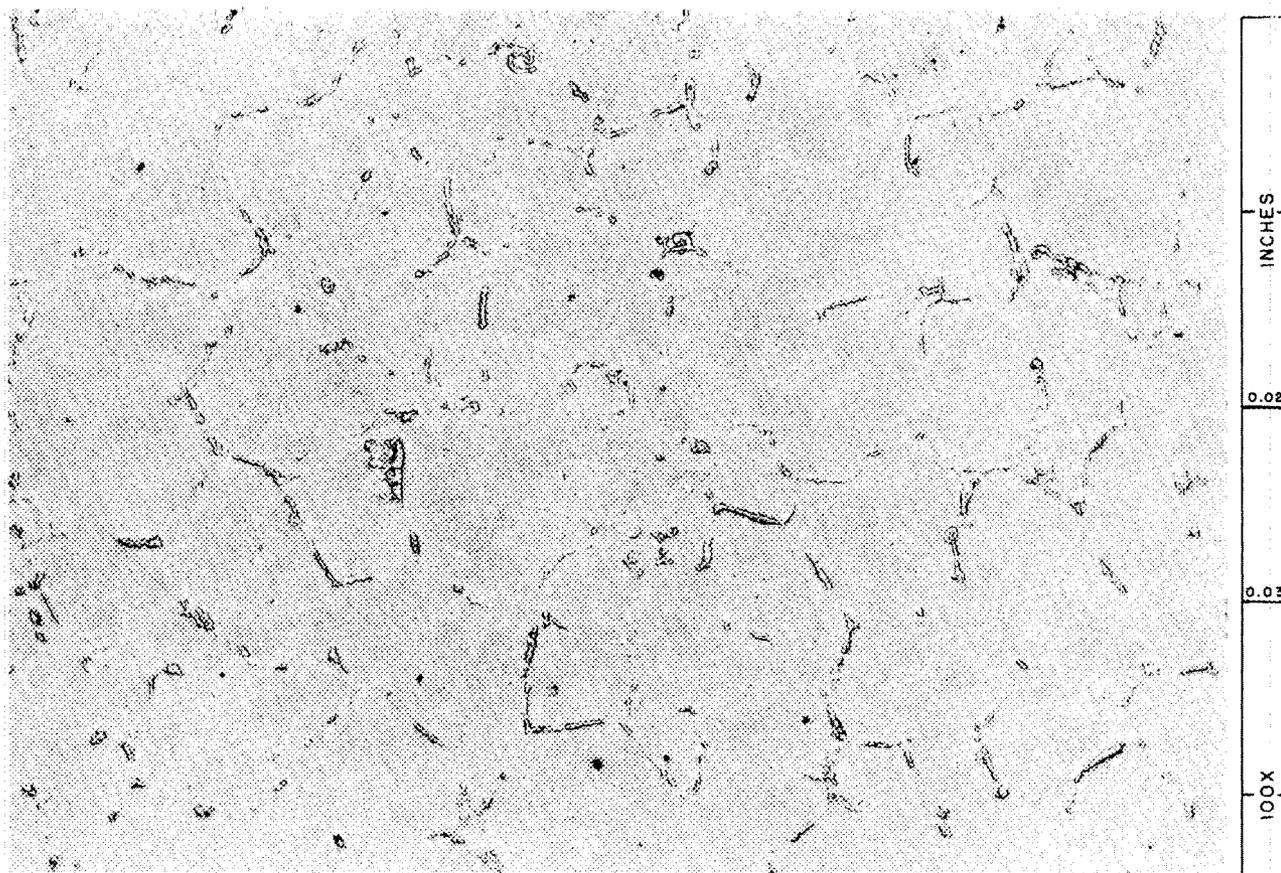


Fig. 4. Photomicrograph of Metallex Thorium Cylinder. 100X.

Retorted for 1-1/2 hours, cold worked to 50% reduction in thickness and vacuum annealed for 1-1/2 hours at 800°C.

The principal visible impurity is thorium carbide.

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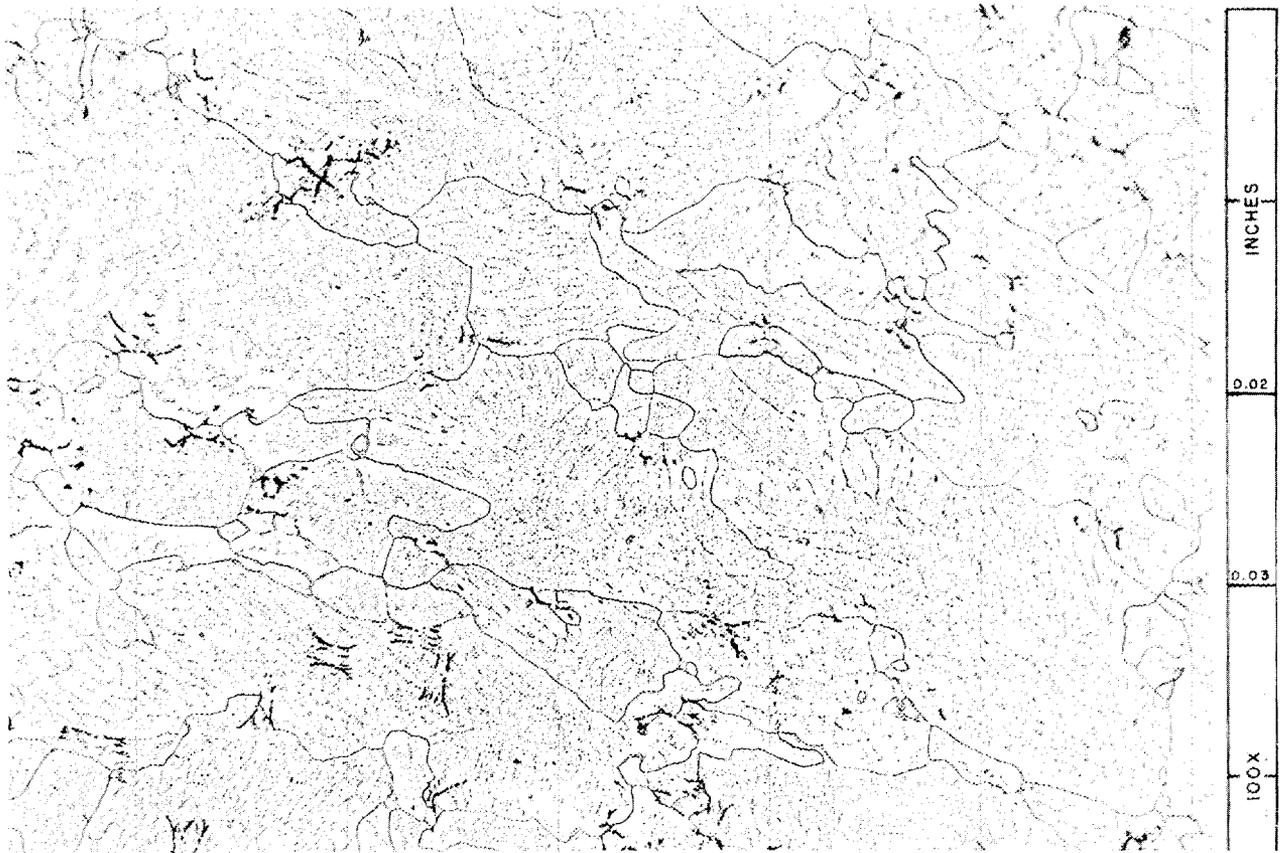


Fig. 5. Photomicrograph of Metallex Thorium Cylinder. 100X.
Retorted 1/2 hour at 1100°C followed by arc melting.

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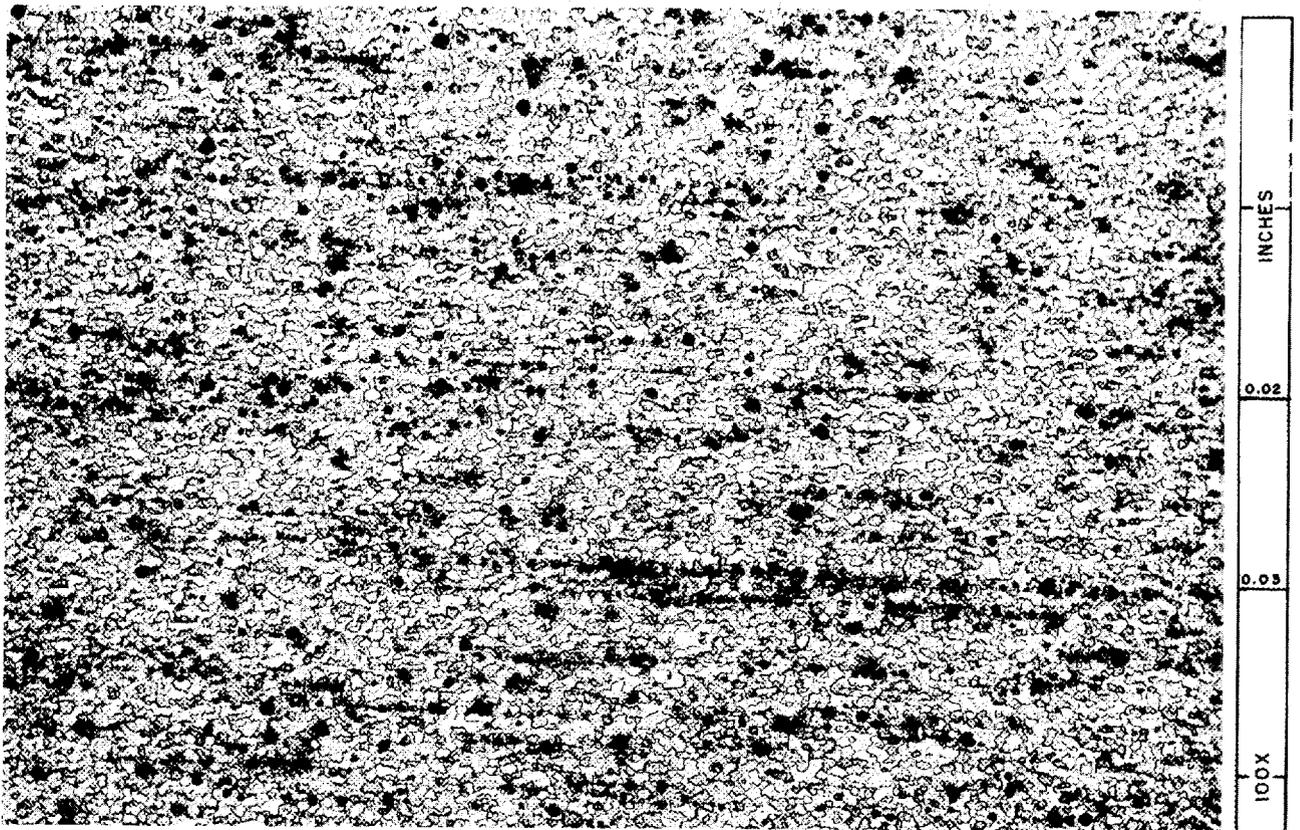


Fig. 6. Photomicrograph of Ames Thorium Metal, 100X.

Cold rolled to 85% reduction in thickness, annealed 1/2 hour at 742°C.

Principal impurity - Thorium oxide.