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## PREPARATION OF METALS BY MAGNESIUM-ZINC REDUCTION

### Part II. Reduction of Thorium Dioxide

by

A. V. Hariharan, J. B. Knighton,  
and R. K. Steunenberg

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## Part II. Reduction of Thorium Dioxide

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## ABSTRACT

The preparation of thorium metal by reduction of thorium dioxide with liquid magnesium-zinc alloy has been investigated on a laboratory scale. The extent of reduction was determined as a function of time, amount and composition of flux, temperature, agitation, particle size of the oxide, and magnesium concentration in the alloy. The rate and extent of reduction were improved by the use of an argon atmosphere, although complete reductions were achieved in an air atmosphere. The reduction rates of thorium dioxide were slower than those obtained with  $U_3O_8$ , but the effects of changes in the flux composition were similar. Under optimum conditions, over 99% reduction of thorium dioxide was obtained in less than 4 hr, and product purities up to 99.7% were achieved. Four small-scale demonstration experiments were performed, in which thorium dioxide was reduced by zinc-magnesium alloy, the resulting liquid-metal solution was distilled to produce a thorium metal sponge, and the sponge was consolidated by arc-melting. It was also shown that thorium tetrafluoride is readily reduced by this method.

## I. INTRODUCTION

The present method for commercial production of thorium metal involves metallocermic reduction of thorium tetrafluoride with calcium in the presence of zinc chloride, which serves as a booster to increase the heat of reaction.<sup>1-4</sup> The thorium tetrafluoride is prepared by precipitation of thorium oxalate from thorium nitrate solution, calcination of the oxalate at 650°C, and hydrofluorination of the resulting thorium dioxide at about 570°C. The product of the reduction is thorium metal alloyed with about 4 to 7 w/o zinc, which is removed by retorting. Various other methods for producing thorium, such as calcium reduction of thorium dioxide, electrolysis of the fluoride, the Kroll process, thermal decomposition of the iodide, and sodium and sodium amalgam reduction of the tetrachloride, have been investigated, but none appears to be as satisfactory as calcium reduction of the tetrafluoride.

The use of magnesium-zinc alloy for the reduction of thorium dioxide has the potential economic advantages of using a much less expensive reductant than calcium, and eliminating the need for a hydrofluorination step. The procedure also appears to be safer than the bomb-reduction method. On the other hand, the technology of the liquid-metal procedure is less developed, and the vacuum-distillation step required to recover the product from the liquid-metal solution is a larger-scale operation than the retorting step used to dezinc the thorium in the present process.

This study was an extension of previous work on the reduction of uranium oxides by magnesium-zinc alloys.<sup>5</sup> The effects of different variables on the reduction rate, as in the uranium study, were determined by their influence on the extent of thorium dioxide reduction as a function of time.

## II. EXPERIMENTAL PROCEDURE

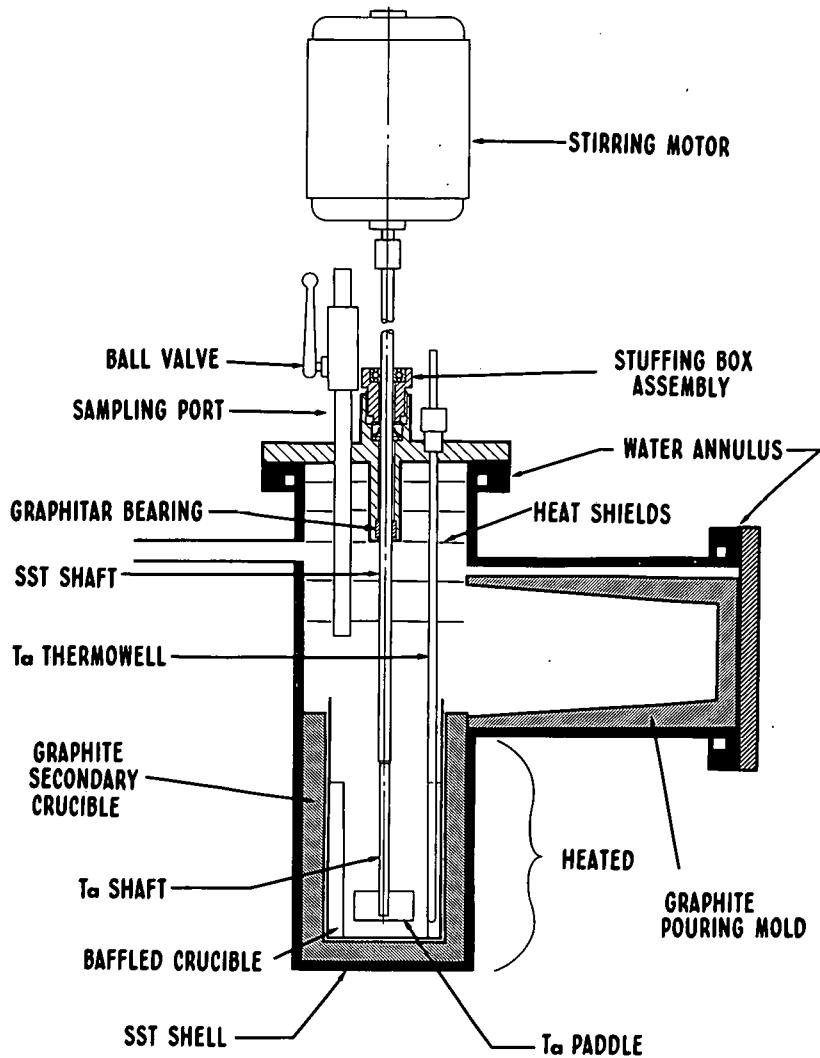
The molten salt fluxes were prepared from anhydrous, reagent-grade salts, except for magnesium chloride, which was obtained as a by-product from the Kroll process used for the production of zirconium. The thorium dioxide, obtained from AEC sources, was a high-fired material (calcination temperature, 1000°C) that had been screened to -325 mesh. The zinc and magnesium were obtained under purity specifications exceeding 99.99 and 99.95%, respectively.

Several preliminary reductions were performed in the open air in apparatus similar to that used for the  $U_3O_8$  reduction studies.<sup>5</sup> The procedure consisted of charging 400 g of zinc-5 w/o magnesium alloy and 200 g of a selected flux (flux:metal volume ratio about 1:1) to a tapered, slip-cast, alumina crucible, placing the crucible in the furnace, and heating to the operating temperature of 750°C. A paddle-type stirrer was then positioned about 3/8 in. from the bottom of the crucible, and the system was stirred at 800 rpm before introduction of the thorium dioxide. In each experiment, the amount of thorium dioxide used was sufficient that complete reduction would produce a final thorium concentration of 1.0 w/o in the magnesium-zinc alloy. After various periods of time, unfiltered samples of the flux and metal phases were withdrawn into 1/4-in.-ID Vycor tubes. The samples were dissolved and analyzed for thorium by a spectrophotometric method involving the use of Thoron reagent.<sup>6</sup>

The preliminary studies were followed by a more systematic investigation in which an argon atmosphere was used. The apparatus, shown in Figure 1, consisted primarily of a resistance-heated, tilt-pour furnace made of Type 304 stainless steel. The reductions were conducted in a tantalum crucible that was equipped with four internal baffles to enhance mixing. The tantalum crucible was located inside a graphite secondary container. A pouring lip on the tantalum crucible extended over a tapered graphite mold, which was maintained at room temperature. By tilting the entire furnace, the molten contents of the tantalum crucible could be poured into the mold. The stirrer was a flat tantalum paddle 1 1/2 in. long by 3/4 in. wide. The furnace was also

equipped with a thermocouple well, a sampling port, and provisions for applying vacuum or an argon atmosphere.

Figure 1  
THORIUM DIOXIDE REDUCTION APPARATUS



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The procedure used for the argon-atmosphere experiments differed somewhat from that used in the preliminary air-atmosphere reductions. The thorium dioxide, along with 300 g of previously melted flux and 570 g of zinc, was charged to the crucible. The charge was gradually heated to 400°C under vacuum; then the system was filled with slightly more than one atmosphere of argon pressure and heated to the operating temperature. The stirring paddle and thermocouple well were then inserted into the melt, 30 g of magnesium was added through the sampling port, and after allowing 5 to 10 min for the magnesium to melt, stirring

was initiated. At suitable intervals, filtered samples were withdrawn into 1/4-in. tantalum tubes that terminated in a tantalum frit with a pore size of 20 microns. At the end of the reduction period, a filtered metal sample and an unfiltered flux sample were taken; then the furnace was tilted 90° to pour the molten alloy and flux into the graphite mold. The rate of reduction was determined from the thorium content of the intermediate liquid-metal samples, and the final extent of reduction was ascertained from the terminal flux and metal samples.

To determine the thorium concentration that could be accommodated by the liquid-metal phase, a brief series of solubility determinations was completed. The solubility of thorium was measured in zinc-magnesium alloys with magnesium concentrations from 2 to 20 w/o at temperatures of 750, 800, and 850°C. The solubility data were obtained by taking filtered samples of the thorium-saturated liquid-metal solutions.

The final experimental work consisted of two pairs of demonstration runs designed to evaluate, on the laboratory scale, a practical scheme for the reduction of thorium dioxide. High-purity zinc and magnesium were employed (zinc, 99.999%; magnesium, 99.95%), and the final thorium loadings in the magnesium-zinc phase upon complete reduction of the oxide corresponded to 6.5 to 9.1 w/o, respectively, in the two runs. The fluxes were purified by premelting in contact with 50 g of zinc-5 w/o magnesium alloy. The thorium-zinc-magnesium solutions resulting from the reductions were retorted under 0.1-mm Hg pressure at 900°C to remove the zinc and magnesium, and the thorium sponge product was consolidated by arc-melting.

### III. RESULTS

#### A. Preliminary Experiments with Air Atmosphere

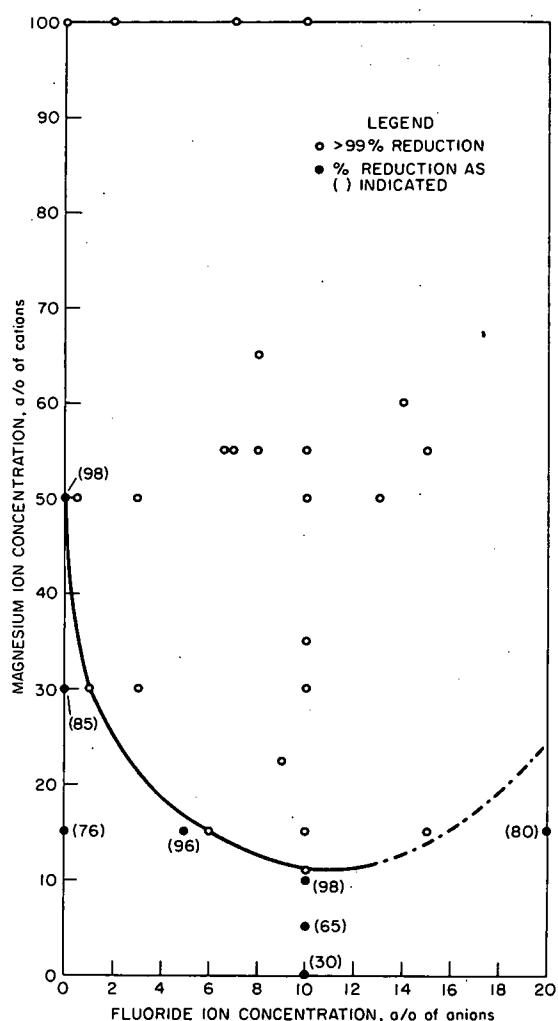
Since the previous work<sup>5</sup> had shown the reduction rate of uranium oxides to be strongly influenced by the flux composition, this variable was investigated at the outset in the thorium dioxide reduction studies. To promote wetting of the thorium dioxide and to encourage a clean, well-defined, flux-metal interface, 5 m/o magnesium fluoride was incorporated into the various fluxes. The preliminary experiments indicated that the reduction rate of thorium dioxide was considerably slower than that observed with  $U_3O_8$ , but the effects of varying the flux composition were quite similar. Magnesium chloride again proved to be an essential ingredient of the flux, and alkali metal chlorides added to the magnesium chloride as diluents resulted in decreasingly effective reductions in the order  $LiCl > NaCl > KCl$ . Fluxes consisting of the systems  $CaCl_2$ - $MgCl_2$ - $MgF_2$  and  $MgCl_2$ - $MgF_2$  became increasingly effective as the magnesium fluoride content was raised from 5 to 20 m/o. Although somewhat less effective than the  $LiCl$ - $MgCl_2$ - $MgF_2$  system, the  $CaCl_2$ - $MgCl_2$ - $MgF_2$  and  $MgCl_2$ - $MgF_2$  fluxes were deemed more practical because of their lower cost, and they were therefore used in the subsequent studies. Reductions in excess of 99.7% were obtained in

180 to 240 min at 750°C under an air atmosphere, using 45 m/o  $\text{CaCl}_2$ -45 m/o  $\text{MgCl}_2$ -10 m/o  $\text{MgF}_2$  and 35 m/o  $\text{CaCl}_2$ -55 m/o  $\text{MgCl}_2$ -10 m/o  $\text{CaF}_2$  as fluxes.

Figure 2

EFFECT OF MAGNESIUM AND FLUORIDE IONS  
ON REDUCTION OF THORIUM DIOXIDE

Temperature: 750°C  
Time: 240 min  
Mixing Rate: 800 rpm  
Metal: 600 g Zn-5 w/o Mg  
Flux: 300 g  $\text{CaCl}_2$ - $\text{MgCl}_2$ - $\text{CaF}_2$  as shown  
Oxide: 6.8 g  $\text{ThO}_2$



below the curve in Figure 2, the reduction rates dropped off sharply with decreasing magnesium ion concentration.

2. Temperature

The data in Table I were obtained from reduction experiments at 750, 800, and 850°C. Temperatures below 750°C were too close to the

It was discovered, however, that faster and more reproducible reductions were possible under an inert atmosphere, and all of the following studies were conducted in an argon-atmosphere furnace.

B. Experiments with Argon Atmosphere

1. Flux Composition

The results of the preliminary experiments indicated that magnesium and fluoride ions in the fluxes had an important influence on the rate and extent of thorium dioxide reduction. To determine the concentrations of these ions required to produce satisfactory reductions, a series of experiments was completed, using  $\text{CaCl}_2$ - $\text{MgCl}_2$ - $\text{MgF}_2$  fluxes of varying composition and an argon atmosphere. The results, shown in Figure 2 in terms of magnesium cation and fluoride anion concentrations, indicate that a definite composition region exists in which the reductions were at least 99% complete in a 240-min period for the conditions used. From a cost standpoint, it would be desirable to use the minimum magnesium and fluoride ion concentrations that would prove satisfactory. At a fluoride concentration of about 10 a/o of the anions, a minimum magnesium cation concentration of about 11 a/o was necessary for complete reduction of the thorium dioxide. Fluxes containing more than 20 a/o fluoride anions were not investigated, since the viscosities were too high for practical operation. In the region

melting point of the flux for practical use, and above 850°C the vapor pressure of the zinc became excessive. The results indicate that the temperature dependence of the reduction rate was small. Complete reduction was achieved in 240 min at all three temperatures, but the initial rate appeared to be faster at the higher temperatures.

Table I  
EFFECT OF TEMPERATURE ON REDUCTION RATE OF THORIUM DIOXIDE

Temperature (°C)	Percent Reduction of ThO <sub>2</sub>			
	60 min	120 min	180 min	240 min
750	53	76	92	99+
800	61	86	96	99+
850	83	92	98	99+

### 3. Agitation

The effect of mixing rate on the reduction of thorium dioxide was investigated in the laboratory-scale equipment by contacting the flux containing the suspended thorium dioxide with the liquid-metal phase at different stirring speeds. The paddle-type tantalum stirrer shown in Figure 1 was operated at speeds ranging from 200 to 1000 rpm in the baffled tantalum crucible. The results in Table II show that the reduction rate of thorium dioxide increased with the stirring speed, and that complete reduction was achieved under these conditions only when the stirrer was operated at a speed of at least 800 rpm. Whereas in the reductions of U<sub>3</sub>O<sub>8</sub> increasing the stirring speed above about 400 rpm had little effect upon the reduction rate, the leveling off of the reduction rate with increased stirring speed was not observed in the case of thorium dioxide at speeds up to 1000 rpm.

Table II  
EFFECT OF AGITATION ON REDUCTION RATE OF THORIUM DIOXIDE

Mixing Rate (rpm)	Percent Reduction of ThO <sub>2</sub>			
	60 min	120 min	180 min	240 min
200	15	30	43	55
400	18	39	47	58
600	51	74	87	96
800	53	76	92	99+
1000	76	98	99+	99+

#### 4. Type and Particle Size of Thorium Dioxide

The reduction rates of thorium dioxide prepared from thorium oxalate by calcination at 350 and 1000°C are compared in Table III. The particle size was 10-15 microns for the 350°C material and 1-2 microns for the 1000°C material, with corresponding BET surface areas of 12 and 16 m<sup>2</sup>/g. There was no significant difference in the reduction rates. Thorium dioxide prepared by a sol-gel process,<sup>7</sup> however, had a slower reduction rate, only 46% being reduced in 240 min under these conditions. This material, which was fired at 650°C, consisted of spherical particles 25 to 50 microns in diameter with a surface area of 4.9 m<sup>2</sup>/g. Although not demonstrated experimentally, it is believed likely that the sol-gel product could be reduced satisfactorily if the magnesium and fluoride ion concentrations in the flux were increased.

Table III

#### EFFECT OF CALCINATION TEMPERATURE ON REDUCTION RATE OF THORIUM DIOXIDE

Temperature: 800°C  
 Mixing Rate: 800 rpm  
 Metal: 600 g Zn-5 w/o Mg  
 Flux: 75.0 m/o CaCl<sub>2</sub>-15.0 m/o  
       MgCl<sub>2</sub>-10.0 m/o CaF<sub>2</sub>  
 Oxide: 6.8 g ThO<sub>2</sub>, calcined at  
       350°C and at 1000°C

Thorium Dioxide Calcination Temperature (°C)	Percent Reduction of ThO <sub>2</sub>			
	60 min	120 min	180 min	240 min
350	73	86	95	99+
1000	61	86	96	99+

#### 5. Thorium Loading

For a practical process, much higher loadings of thorium dioxide starting material in the flux and of thorium metal product in the zinc-magnesium phase would be necessary to decrease the process volumes. To determine the final thorium concentration that could be accommodated in the metal phase, reductions were performed with increasing amounts of thorium dioxide to produce thorium concentrations approaching 9.1 w/o in the zinc-magnesium solution. Reductions were conducted for 240 min with 600 g of zinc-magnesium alloy and 300 g of flux at a temperature of 800°C and a stirring speed of 800 rpm. Since the resulting concentrations of thorium in the metal phase frequently exceeded its solubility at 800°C, the degree of reduction

after 240 min was determined by dissolving the entire flux and analyzing the solution for thorium. The results are summarized in Table IV. These data show that the main consequence of increasing the thorium loading in the system was that higher magnesium chloride concentrations in the flux were required for satisfactory reduction.

Table IV  
EFFECT OF THORIUM LOADING ON REDUCTION RATE OF THORIUM DIOXIDE

Temperature: 800°C  
Time: 240 min  
Mixing Rate: 800 rpm  
Metal: 600 g Zn-5 w/o Mg  
Flux: 300 g CaCl<sub>2</sub>-MgCl<sub>2</sub>-10.0 m/o  
CaF<sub>2</sub> (MgCl<sub>2</sub> content as shown)  
Oxide: ThO<sub>2</sub> - 325 mesh, calcined at 1000°C

Final Thorium Concentration in Zn-Mg on Complete Reduction (w/o) <sup>a</sup>	Percent Reduction of ThO <sub>2</sub>				
	15 m/o MgCl <sub>2</sub>	29 m/o MgCl <sub>2</sub>	25 m/o MgCl <sub>2</sub>	30 m/o MgCl <sub>2</sub>	47.5 m/o MgCl <sub>2</sub>
0.99	99	-	-	-	-
2.91	99	-	-	-	-
4.76	95	99	-	-	-
6.54	-	89	96	97	-
9.09	-	-	93	93	98

<sup>a</sup>Based on the ternary Zn-Mg-Th alloy.

In another series of experiments, the effect of magnesium chloride concentration on the extent of reduction was investigated, using thorium loadings that would produce 9.1 w/o thorium in the metal phase upon complete reduction. In this case, a zinc-10 w/o magnesium alloy was used. Under these conditions, a magnesium chloride concentration of nearly 50 m/o was needed to achieve reductions exceeding 99%.

The effect of thorium dioxide loading in the flux on the extent of reduction was investigated in a series of experiments in which the weight ratio of thorium dioxide:flux was varied from 0.12 to 0.46. The system, consisting of 600 g of zinc-5 w/o magnesium alloy, flux, and thorium dioxide, was heated to 850°C and agitated at a mixing rate of 800 rpm for a period of 240 min. The flux composition was 90 m/o MgCl<sub>2</sub>-10 m/o MgF<sub>2</sub>. The magnesium content of the liquid-metal phase ranged from about 8 to 15 w/o.

To achieve reductions in excess of 97.5% with a final thorium concentration of approximately 12 w/o in the liquid-metal phase, a thorium dioxide:flux weight ratio of less than about 0.22 was required. Attempts to produce final thorium concentrations in excess of 12 w/o with reduction yields over 97.5% were unsuccessful.

## 6. Magnesium Concentration

The effect of magnesium concentration in the zinc alloy on the reduction of thorium dioxide was investigated in a series of 240-min reductions at 800°C with a stirring rate of 800 rpm, and a final thorium concentration of 9.1 w/o in the alloy upon complete reduction. The magnesium concentration was varied from 1 to 50 w/o. Filtered samples of the liquid-metal phase

were taken at the end of the 240-min period and analyzed for thorium<sup>6</sup> and magnesium.<sup>8</sup> The flux phase was analyzed for unreduced thoria. The results for three different flux compositions are presented in Figure 3. With increasing magnesium concentration, the extent of reduction rose sharply, reaching a maximum at about 8 w/o magnesium, then fell off gradually. The optimum magnesium concentration for process use appears to be between about 5 and 15 w/o.

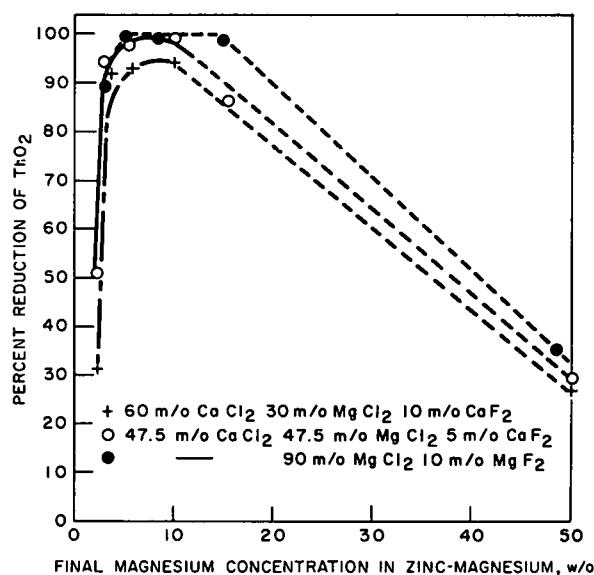
### C. Small-scale Process Demonstrations

The results of the preceding experiments seemed sufficiently encouraging to warrant a small-scale demonstration of a conceptual process for the preparation of thorium, in which thorium dioxide was reduced and a consolidated metallic product was obtained. A schematic flowsheet showing the steps involved in the procedure is illustrated in Figure 4. Two pairs of runs were completed, in which the final thorium concentra-

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tions in the metal phase would be 6.5 and 9.1 w/o upon complete reduction. In each pair of runs, the same crucible was used in an attempt to determine if a continuing buildup of thorium would occur because of incomplete pouring of the liquid-metal phase when the reduction step was completed.

The reduction yields and overall material balances are listed, along with the operating conditions in Table V. In all four reductions, the solidified flux and metal that had been poured into the graphite mold were readily separated, yielding bright ingots of thorium-zinc-magnesium alloy. The thorium metal sponge obtained by retorting the ingots was a light-gray color and contained fine crystals. Consolidation of the sponge by arc-melting resulted in



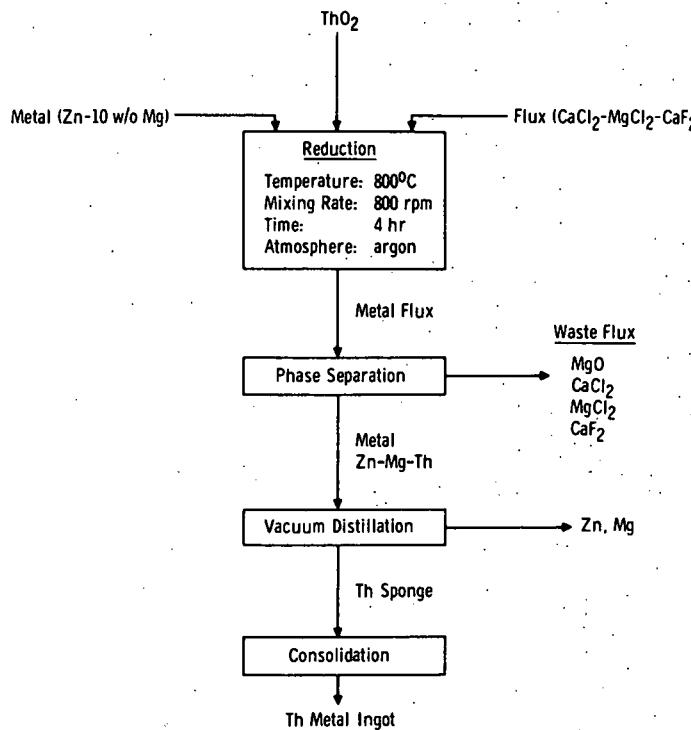


Figure 4  
PREPARATION OF METALLIC THORIUM

Table V  
LABORATORY DEMONSTRATION OF THORIUM DIOXIDE REDUCTION

	Runs IA and IB	Runs IIA and IIB
<u>Conditions</u>		
Temperature	800°C	800°C
Time	240 min	240 min
Mixing Rate	800 rpm	800 rpm
Atmosphere	argon	argon
Crucible	tantalum	tantalum
Metal Charge		
High-purity zinc	570 g	540 g
High-purity magnesium	39 g	73 g
Flux Charge		
Weight	300 g	300 g
CaCl <sub>2</sub>	60 m/o	47.5 m/o
MgCl <sub>2</sub>	30 m/o	47.0 m/o
CaF <sub>2</sub>	10 m/o	5.0 m/o
Thorium Dioxide Charge		
Weight	47.8 g	68.3 g
Final conc'n in Zn-Mg sol'n <sup>a</sup>	6.5 w/o	9.1 w/o
Pouring Temperature <sup>b</sup>		
<u>Results</u>		
Run No.	IA	IB
Percent reduction	97%	93%
Pouring yield <sup>b</sup>	92%	93%
Weight of Th remaining in crucible <sup>b</sup>	-	9.8 g
Weight of Th metal sponge	37.5 g	32.6 g
Weight of arc-melted ingot	36.2 g	32.5 g
Amount recovered as product	86%	78%
Thorium material balance	-	98.6%
		91%
		95%
		99.9%

<sup>a</sup>Assuming complete reduction.

<sup>b</sup>Flux and metal phases were poured into a graphite mold at the end of the reduction period.

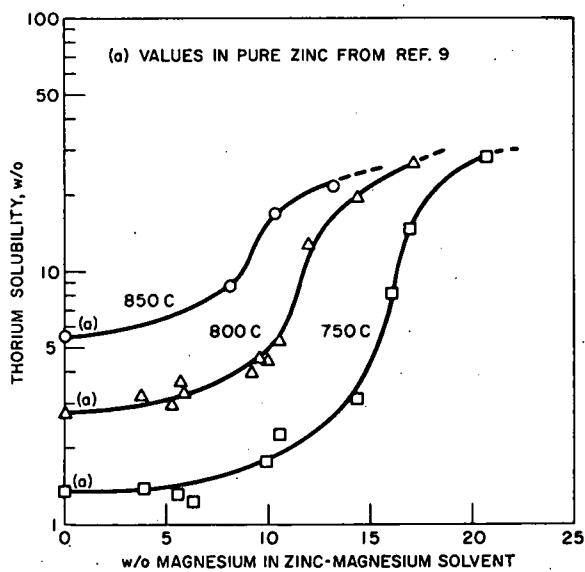
silvery-white buttons, which retained their luster even after long periods of exposure to the laboratory atmosphere.

In Runs IA and IB, the reduction yields were 97 and 93%, with consolidated metal yields of 86.1 and 77.5%. When the magnesium concentration in the metal was increased from 5 to 10 w/o and the magnesium chloride content of the flux was increased from 30 to 47.5 m/o in Runs IIA and IIB, the reduction yields increased to 99 and 98%. Final recoveries of metallic product in Runs IIA and IIB were 90.7 and 94.7%. The only major losses resulted from incomplete pouring of the liquid metal from the crucible after reduction, which appears to be a problem characteristic of the small scale of the operation.

The metallic impurities in the product were determined by spectrochemical analysis, and the nonmetallic impurities by standard chemical

methods. Overall purities of the arc-melted products were between 99.70 and 99.85%. With further operating experience and more suitable equipment and techniques, it is reasonable to expect that purities of 99.90% could be readily achieved with this method.

Figure 5  
SOLUBILITY OF THORIUM IN MAGNESIUM-ZINC SOLUTIONS

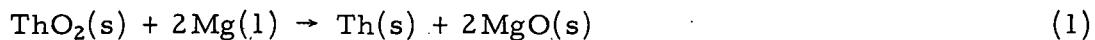


#### D. Solubility of Thorium in Magnesium-Zinc Solutions

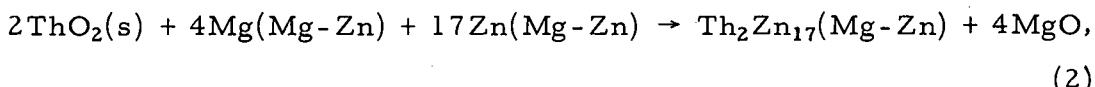
Determinations of the solubility of thorium in magnesium-zinc solutions were made at temperatures of 750, 800, and 850°C, and at magnesium concentrations up to about 20 w/o. The results are shown in Figure 5. With increasing magnesium concentration, the solubility of thorium remained nearly constant at first, then increased sharply. The solubility was also rather strongly dependent upon the temperature. These data indicate that many of the reduction experiments were performed under conditions in which thorium was being precipitated from the liquid-metal phase as a thorium-zinc intermetallic compound.

#### IV. DISCUSSION

The standard free energy of the reaction



is reported to be +13 kcal at 1000°K, indicating that magnesium reduction of thorium dioxide would not be feasible. In a zinc-rich solution, however, thorium forms the intermetallic compound  $\text{Th}_2\text{Zn}_{17}$ , which has a free energy of formation of -73 kcal/mole.<sup>9</sup> Formation of the thorium-zinc intermetallic compound in a magnesium-zinc solution results in the following overall reaction:



for which the free-energy change is -47.0 kcal at 1000°K (neglecting the free energies of dilution of the metallic reactants and products). Thus, magnesium alone is incapable of reducing thorium dioxide, but the reaction becomes feasible in zinc solutions of magnesium because of the additional driving force provided by the thorium-zinc interaction. In this regard, the curves shown in Figure 3 are of interest. At very low magnesium concentrations, the reduction yields are low because insufficient magnesium is present to drive reaction (2) in the forward direction in accordance with the mass-action effect. As more magnesium is added, the reaction proceeds and is aided by the additional free energy supplied by the formation of  $\text{Th}_2\text{Zn}_{17}$ , which is reflected as a low-activity coefficient for thorium in zinc-rich solutions. Upon further magnesium addition, however, the activity coefficient of thorium is increased by the larger proportion of magnesium present, with the result that reaction (2) tends to be inhibited. The maxima in the curves at about 8 w/o magnesium in Figure 3 are a consequence of these two competing effects. The same general behavior has been observed during determinations of the distribution coefficients of thorium between magnesium-zinc solutions and magnesium chloride, where no oxides were present.<sup>10</sup>

The mechanism of the reduction reaction was not investigated specifically. The relatively slow reduction rates and the strong dependence of the rates on the flux composition, however, suggest that the rate-controlling step may be a thorium dioxide-flux reaction. As in the case of uranium, thorium tetrafluoride was very rapidly reduced under the same conditions.

## V. CONCLUSIONS

From a practical viewpoint, the direct reduction of thorium dioxide by magnesium-zinc alloys may represent a technically feasible process for the production of thorium metal. The economic potential was not evaluated. Relatively inexpensive reagents are used for the metal and flux phases, and metal of acceptable quality can be produced in good yield. Recycle of the zinc and magnesium from the retorting step of the process is desirable, not only to conserve these materials, but also to minimize the impurities that would be introduced with additional zinc and magnesium. Although tantalum equipment was used successfully in the laboratory-scale studies, other work in a similar system indicated that some tantalum contamination of the product may occur. Tungsten or ceramic crucibles, or vessels lined with these materials would probably prove more satisfactory for a practical process and would contribute no significant impurities to the product. Optimum reduction conditions were found at a temperature of about 800°C, an inert atmosphere, a magnesium concentration of 5 to 10 w/o in the zinc phase, a flux containing a large proportion of magnesium chloride and approximately 10 m/o calcium or magnesium fluoride, and a thorium dioxide:flux weight ratio of about 0.22. Thorium loadings up to about 12 w/o in the metal phase at the completion of the reduction appear to be feasible.

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## REFERENCES

1. F. L. Cuthbert, Thorium Production Technology, Addison-Wesley Publishing Co., Reading, Mass., p. 146 (1958).
2. The Metal Thorium, Proceedings of the USAEC-ASM Conference on Thorium, Cleveland, Ohio, American Society for Metals (1958).
3. Thorium-U<sup>233</sup> Symposium, BNL-483 (C-26)(1958).
4. F. H. Spedding, H. A. Wilhelm, W. H. Keller, J. E. Iliff, and C. Neher, The Production of Thorium Metal by the Metallothermic Reduction of Thorium Fluoride, CT-2950 (1945).
5. J. B. Knighton and R. K. Steunenberg, Preparation of Metals by Magnesium-Zinc Reduction. Part I. Reduction of Uranium Oxides, ANL-7057 (June 1965).
6. P. F. Thomason, M. A. Perry, and W. M. Byerly, Determination of Microgram Amounts of Thorium, Anal. Chem. 21, 1239 (1949).
7. C. E. Crouthamel, W. G. Knapp, S. B. Skladzien, and J. W. Loeding, Preparation of High-density, Spherical Thorium Oxide Particles with up to 10 Atom Percent Uranium, ANL-6340 (1961).
8. I. M. Kolthoff and P. J. Elving, Treatise on Analytical Chemistry, Part II, 3, Interscience Publishers, New York, p. 83 (1961).
9. P. Chiotti and K. J. Gill, Phase Diagram and Thermodynamic Properties of the Thorium-Zinc System, Trans. Met. Soc. AIME 221, 573 (1961).

