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SUMMARY REPORT ON THORIUM METAL QUALITY FOR PRODUCTION REACTOR USE

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ABSTRACT

Background material leading to the development of the metal quality of reactor-grade thorium is given. The metal should be sound and of uniform hardness, free of internal cracks and inclusions, and corrosion resistant. It should contain only small amounts of natural uranium, thorium oxide, and elements that act as reactor poisons.

Because of their effect upon metal quality, various methods for the production of thorium are discussed. Use of consumable electrode arc melting as the final step has contributed much to the production of thorium of excellent quality for reactor use.

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SUMMARY REPORT ON THORIUM METAL QUALITY FOR PRODUCTION REACTOR USE

INTRODUCTION

Over the last ten years there have been several periods of interest in thorium as a source of isolatable uranium-233. In 1947, due to the scarcity of uranium supplies, thorium was looked upon as a potential major source of fuel for atomic power reactors. About 1951 there was a revival of interest in thorium for use in the Materials Testing Accelerator (MTA) as well as in reactors. There was another revival of interest three years later.

As a result of the earlier interest, development work was carried out to produce thorium metal, particularly to meet requirements for the MTA. This work was done at the Ames Laboratory of Iowa State College and at the Battelle Memorial Institute. Some of the metal produced in this program was irradiated at the Hanford Atomic Products Operation Plant. Essentially all thorium irradiations before 1955, except for small quantities of thorium carbonate, were made with thorium metal produced at the Ames Laboratory by the calcium reduction of thorium tetrafluoride, a process developed at Ames. For the last period of interest covered in this report, the metal employed was made mainly at the new Fernald Thorium Pilot Plant and irradiated at the Savannah River Plant.

In 1954, when the responsibility for developing thorium elements of optimum quality and shape for irradiation in production reactors and for determining the behavior of the elements upon irradiation was given to the Atomic Energy Division of the du Pont Company by the Atomic Energy Commission, it seemed advisable to review the methods by which thorium metal had been obtained and the quality of the metal that had been produced. As work progressed on the fabrication of thorium elements, the quality of metal required for reactor use became better understood and modifications were made in the processes in order to produce metal to meet these requirements.

The thorium elements considered for fabrication and irradiation were unbonded slugs, bonded slugs, and finally, tubes. Canning methods developed for these elements included die sizing, Al-Si canning, hot-press canning, and coextrusion.

SUMMARY

Reactor-grade thorium should be sound and of uniform hardness; it should be free of internal cracks and inclusions; its corrosion resistance to the reactor environment should be high; the natural uranium content and the amounts of reactor poisons, i.e., elements of high cross section, should be low; and its dissolution should present a minimum problem in the separations processing.

A low thorium oxide content is one of the most important requirements of reactor-grade thorium. Preferred methods of fabrication of several shapes of thorium elements, particularly coextrusion, require a clean, soft metal, and thorium oxide seems to be one of the factors contributing to the hardness of the metal. The thorium oxide is insoluble in most solvents and if undissolved would result in product losses in the separations process for the isolation of uranium-233. The only known solvent for the oxide is a boiling mixture of nitric and hydrofluoric acids. Though it is possible to use such a mixture in quartz vessels on a laboratory scale, the problem of finding a material that can satisfactorily resist such an environment on a production basis has not yet been solved.

Thorium of good quality can be fabricated either by rolling or extrusion, but it has been shown that with metal of poor quality, ingots that cannot be fabricated satisfactorily by rolling to size can be fabricated by extrusion.

The only metal that has been produced to date on a substantial scale is that produced by the consumable electrode arc melting process at Fernald. It has a satisfactory oxide content and a hardness level that makes it possible to coextrude tubular elements with aluminum cladding. It is considered suitable for any type of reactor irradiation, at least in the case of virgin metal. Thorium elements made from recycled metal, that is, machine turnings, croppings, etc. were not irradiated at the Savannah River Plant since, for the period covered by this report, satisfactory methods for remelting recycled metal had not been developed to the point where there was not a considerable increase in the thorium oxide content.

Canned bonded elements were shown to be superior to canned unbonded elements in corrosion tests in steam. It is assumed that they would be superior under irradiation also but there has been no reactor failure with bonded systems with which to compare the failures in unbonded systems. Thorium has shown excellent dimensional stability during irradiation.

DISCUSSION

METAL QUALITY REQUIREMENTS

The metal quality requirements of reactor-grade thorium are determined by five basic factors: (1) the mechanical properties required for the particular reactor shapes, (2) the corrosion behavior in the reactor environment, (3) the effect of reactor poisons, and, in the case of isolation of uranium-233, (4) the separations requirements, and (5) the isotopic purity required in this product.

MECHANICAL PROPERTIES

When the reactor shape is in the form of a short, cylindrical slug the actual mechanical properties of the thorium metal are not critical, but sound metal, with a minimum of inclusions, should be used. Internal cracks and excessive inclusions may lead to premature rupture upon irradiation. Uniform hardness is important if hot pressing is employed to can the slugs.

The mechanical properties of the metal for tubular shapes are, however, much more critical. Again the requirement for sound metal, with a minimum of inclusions, is applicable. In addition, the lowest possible hardness is required for the successful application of the coextrusion fabrication process for cladding with aluminum.

CORROSION BEHAVIOR

In the event of an element failure during irradiation the corrosion behavior of the thorium core becomes of importance. The quality of both the metal and any bond between cladding and core significantly affects corrosion behavior. Segregated impurities and metal quality defects, such as internal cracks that reach the thorium surface, permit corrosion to proceed more rapidly and cause the thorium to swell and perhaps even split due to the buildup of corrosion products. The manner in which corrosion proceeds is at least somewhat dependent upon whether the element is bonded or not bonded. For example, when an aluminum-clad, unbonded, thorium element that has been purposely defected is exposed to 175°C steam, general swelling over the entire surface occurs.(1) A defected bonded element, on the other hand, exhibits only local swelling at the defect when subjected to the same test. Exposure to 175°C steam is used for out-of-pile testing to detect defectively clad elements.

PILE POISONS

The high cross section elements that are most likely to be found in thorium are boron and the rare earths. In relatively small amounts these elements may result in an uneconomic loss of product. In addition, if the high cross section rare earths are present in excessive amounts, they may cause an excessive reactivity change in the reactor within two weeks after startup due to their burning out.

SEPARATIONS REQUIREMENTS

From the separations standpoint one of the most important requirements of a process to isolate uranium-233 from irradiated thorium is a low thorium oxide content in the thorium metal. In the normal dissolving solution for thorium, a mixture of nitric and hydrofluoric acids, a substantial fraction of the thorium oxide content remains undissolved with a corresponding loss of U^{233} product. Although it is possible to dissolve this residue by means of higher acid concentrations and higher temperatures, the resulting equipment corrosion problems are so serious that the Savannah River separations personnel, at least, do not feel that such a procedure is practical on a production basis.

ISOTOPIC PURITY OF FINAL PRODUCT

Whenever pure uranium-233 is the final product desired from irradiated thorium, natural uranium contamination must be kept to a minimum. Fifty ppm of uranium in the thorium will result in 5% U^{238} in the final product when the thorium is exposed to a 1000 g/t level.

The specific thorium metal quality requirements that were developed to ensure satisfactory fabrication and irradiation behavior are described later.

MAJOR REDUCTION PROCESSES

SOURCE OF ORE

The principal source of thorium metal has been monazite sand from India or Brazil. After concentration, the ore generally contains about 5 to 7% ThO_2, 60% rare earth oxides, 26% P_2O_5, 2 to 7% SiO_2, and 0.2 to 0.3% uranium. Sands from Idaho similarly concentrated contain only 3 to 4% ThO_2. Obviously, the thorium will contain some small quantities of the rare earths and uranium.

Although the Atomic Energy Commission has done considerable development work on processing thorium concentrates, essentially all metal produced for reactor use has been made from thorium nitrate tetrahydrate (TNT) obtained from commercial sources.

AMES PROCESS

The basic thorium reduction process used by the Atomic Energy Commission was developed at the Ames Laboratory of Iowa State College and until 1954 all metal production was at this site. Briefly, the Ames process(2) consists of precipitating thorium oxalate by the addition of oxalic acid or ammonium oxalate to a solution of acidified thorium nitrate. The oxalate precipitate is filtered, washed, dried, and then calcined in an oxidizing atmosphere. The oxide is hydrofluorinated at about 550°C in an anhydrous HF atmosphere. The thorium fluoride is mixed with high purity redistilled calcium and anhydrous zinc chloride and fired in a steel reduction bomb, lined with electrically fused dolomite. A biscuit (weighing about 50 lb) of a relatively low melting alloy of thorium and zinc forms at the bottom of the bomb. It is subsequently subjected to a vacuum distillation at 1100°C to remove the zinc. The thorium sponge which remains is melted by induction heating in a beryllia crucible and cast into a graphite mold using a bottom pouring technique. It is then cast into ingots. With the exception of some rectangular ingots cast for MTA use, the ingots cast at Ames were approximately 3-1/2 inches in diameter and 36 inches long and weighed about 100 lb.

FMPC PROCESS

When interest in thorium was revived in 1951, a pilot plant was designed for construction at the Feed Materials Production Center, Fernald, Ohio (FMPC). Prior to completion, however, interest waned again and the plant was not run in until the 1954 cycle started. The process contemplated for the FMPC pilot plant was a modification of the Ames process in three important respects.[2,3] These were:

1. Preparation of the thorium tetrafluoride by direct precipitation with hydrofluoric acid from an acidified thorium nitrate solution.

2. Combination of the de-zincing and melting steps in one piece of equipment.

3. Use of top pour zirconia crucibles rather than bottom pour beryllia crucibles for melting and casting.

4. The reduction and casting steps were scaled up to produce 100-pound biscuits and 400-pound ingots approximately 7 inches in diameter.

With the exception of the increase in size of the biscuits and ingots, the modifications did not prove to be satisfactory. The direct precipitation of the fluoride from a thorium nitrate solution had been looked upon as a definite process improvement, as it would replace the oxalate precipitation, calcining, and hydrofluorination steps. Cost savings in process materials would also be significant. Unfortunately, very serious corrosion and maintenance problems arose and maintenance costs probably exceeded the savings in raw materials. Furthermore, with the attendant corrosion difficulties, significant quantities of iron, chromium, and nickel were picked up and resulted in large undesirable quantities of a second phase in the final metal. This phase was definitely established later to be made up of eutectics with one or more of these impurities.

The combination de-zincing and melting step did not prove to be satisfactory although development work at the National Research Corporation, Cambridge, Mass., had shown some promise. The basic reason for the failure of the combination step was due to the large volume of zinc that had to be distilled.

Top pour zirconia crucibles had been chosen to replace bottom pour beryllia crucibles on the basis of economic considerations, health hazard of beryllium oxide, and process simplification. Almost from the start of operations, however, the melting and casting step was beset with difficulties. Some of these difficulties, if not all, resulted from improper control of processing conditions in earlier steps; for instance, inadequate de-zincing meant that long holding times were required in the zirconia crucibles until the distillation of impurities was completed. Distillation of zinc and calcium resulted in the frequent shorting out of the induction coils inside the vacuum furnace and collection of the zinc and calcium on the pouring spout of the zirconia crucible made it difficult to pour clean metal into the casting mold.

These difficulties unfortunately affected final metal quality as well as processing conditions. Ingot surface and soundness were poor and oxide content and hardness level were high compared with metal produced at the Ames Laboratory. That these factors were not inherent in the melting and casting process was shown by the fact that some material of satisfactory quality was made though not reproducibly.

Although FMPC personnel believed that induction melting in zirconia crucibles could be made practical, because of the urgency of the thorium program at that time, steps were taken to determine the feasibility of consumable electrode arc melting of de-zinced thorium biscuits. A development program at the U. S. Bureau of Mines at Albany, Oregon, initiated and supported by FMPC,(4) proved arc melting to be a much more satisfactory method than induction melting and the increased cost of melting seemed justified. The oxide content and hardness of arc-melted metal fell to levels as low or lower than that of Ames metal. Arc melting was done at the Bureau of Mines on a crash program basis until suitable facilities could be installed at FMPC. These were completed by the summer of 1955.

During 1955, melting procedures for consumable electrode arc melting at both the Bureau of Mines and FMPC did not result in very high metal yield because of the inefficient methods which were used of necessity in the preparation of the electrodes. De-zinced biscuits were cut by band or power saw and the resulting pieces were manually welded together in an inert atmosphere.

Later it was found by FMPC(5) that it was possible to crush the dezinced biscuits into sizes suitable for cold compacting into consumable electrodes. Although not tried on a production scale, experiments have shown this method to be satisfactory and to give a much higher metal yield.

One word of caution should be stated regarding health hazards in the arc melting of thorium, though the same caution is applicable to vacuum induction melting and, to a lesser degree, to other steps in the process involving high temperatures. Most of the radioactivity in thorium originates not from the thorium itself, but from its many daughter decay products. Starting with pure thorium metal, the daughter products will build up to approximately maximum radioactivity in about ten days. During the arc melting operation most of the high activity daughter products are volatilized from the thorium and any dust that collects as a result of the operation is usually highly radioactive, although only for a short time, whereas the activity of the metal itself is rather low. Within about ten days, the "dust" activity has greatly diminished while the bulk metal activity is back to normal again.

The same thing is true for thorium biscuits. If biscuits are dezinced immediately after reduction, biscuit activity is quite low. A beta-gamma count at this time will be meaningless one week or ten days later as the daughter activity will then have built up to several times that of the original reading.

OTHER REDUCTION PROCESSES

Because of the fluctuating interest in thorium, thorium technology did not advance as rapidly as it might have otherwise. However, in addition to the processes used at Ames and at Fernald, other processes were being developed in the hope of obtaining better metal at lower cost. The developments have been essentially completed except for obtaining irradiation data. No decision has been reached, however, on whether any of the alternative processes will replace the calcium reduction of the fluoride since the demand for thorium has again waned.

Development work has been done on five alternative reduction methods. These methods and the sites performing the work are as follows:

1. Electrolytic reduction of thorium tetrachloride(6) - Horizons, Inc., Cleveland, Ohio.
2. Magnesium reduction of thorium tetrachloride(7,8) - Bureau of Mines and Ames Laboratory, Ames, Iowa.
3. Sodium reduction of thorium tetrachloride(9) - Oak Ridge National Laboratory, Oak Ridge, Tennessee.

4. Calcium reduction of thorium oxide(10) - Sylvania Electric Products, Inc., Bayside, N. Y. (now Sylvania-Corning Nuclear Corporation).

5. Electrolytic reduction of thorium oxide - Savannah River Laboratory, Aiken, S. C. (see DP-205 by L. H. Meyer).

These alternative methods are described fully in the references given, and only a few brief comments will be made here. First of all, it should be noted that three of the five methods involve the use of thorium tetrachloride as a starting material and two the use of thorium oxide. None of the processes results in massive thorium but rather in metal ranging from a very fine powder to a porous sponge. The oxide reduction with calcium appears to be the cheapest and simplest, but the resulting finely divided powder may be hazardous. In fact, a very serious accident occurred upon completion of the oxide reduction program when some of the residues were being oxidized for safe storage.(11) However, the other methods, including calcium reduction of the fluoride, are not immune to accidents as evidenced by the serious fire which occurred at Fernald during the blending of thorium fluoride, calcium metal, and zinc chloride, preparatory to the reduction step.(12) All of the five processes appear capable of producing thorium metal that is as satisfactory as that produced by the calcium reduction of the fluoride, at least with respect to over-all chemical purity. Restrictions on some elements not normally analyzed for in metal produced by the fluoride process may, however, be required, e.g., hydrogen and chlorine in electrolytic metal.

COMPARISON OF METAL PRODUCED BY THE AMES, FMPC INDUCTION MELTING AND FMPC ARC MELTING PROCESSES WITH TARGET REQUIREMENTS

The basic requirements for reactor-grade thorium have already been given. A comparison will now be made of the quality of metal produced by the three variations of the same basic process,(2,3,13) namely: Ames thorium, thorium induction melted at FMPC, and thorium arc melted at FMPC, on the basis of (1) chemistry of impurities, (2) ingot quality, (3) fabrication characteristics, and (4) properties of fabrication rod.

CHEMISTRY OF IMPURITIES

The chemical limits to meet the basic metal quality requirements were recommended by the Thorium Quality Working Committee of the Metallurgy Development Advisory Committee, and are listed in the table on page 14.

	Desired Chemical Requirements	Ames Metal	FMPC Induction-Melted Metal	FMPC Arc-Melted Metal	Latest FMPC Arc-Melted Metal
Oxide	1% Max.	1.25% Avg.	2.5%	1.5% Avg.	<1% Avg.
	(ppm-max.)	(ppm)	(ppm)	(ppm)	(ppm)
C	400	300-800	250-600	<300	80
N	150	85-155	150-450	<300	120
Al	25	<25	100-400	<200	<10
Ca	70	<70	100	<100	75
Mg	20	<20	10	<20	
Si	50	<50	30-100*	<50	
Fe	100	35-115	>600	<500	85
Ni	50		>600	<500	15
Cr	50		220	<200	15
Cu	50		125	<200	10
Zn	100	<20	<10	<500	60
B	1	<1	2	<1	<0.2
Cd	0.5	<0.5	<0.5	<0.5	
Gd	0.2		<5	<5	2.5
Sm	0.1			<2	
Dy	0.5			<2	
Eu	0.5			<2	
U	25			<10	<10
Zr			2500		

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* 20% of ingots had values of approximately 600 ppm Si.

Production experience with arc-melted metal has shown that these requirements can be met. Limits on some chemical impurities, however, undoubtedly can be relaxed, and suggested modifications to these limits are included in the following discussion.

The desired chemical requirements (second column of preceding table) were based in part on analyses of Ames production metal. The Ames metal quality (Column 3) was obtained by reviewing all virgin ingot analyses for over six months of production. The range indicated for each individual impurity covered in most cases over 80 to 90% of the total number of such ingots.

Oxide analyses, although meager, were consistently about 1.25%. So far as known, no attempt was made at Ames to minimize the oxide content and it was felt that it could be kept well below 1%.

Carbon was the only impurity that was specified at a significantly lower level than was present in Ames metal. The lower limit was desired since it had been established that carbon had the most potent hardening effect of any impurity. Other impurities may have had an effect on hardness, but this was masked by the stronger effect of carbon.

When the FMPC pilot plant started up, using induction melting of biscuits that had been reduced from fluoride prepared by the HF precipitation from a nitrate solution, the general level of impurities (particularly oxide, nitrogen, and the "corrosion products", Fe, Cr, Ni, and Cu) was considerably higher than in Ames metal. The oxide and "corrosion products" contributed significantly to additional phases in the thorium microstructure with the result that the hardness level was also considerably higher. The "corrosion products" also concentrated at grain boundaries (as would be expected for relatively low melting eutectic constituents) and this contributed to embrittlement of the metal. Attempts were made to correlate hardness values with specific impurities, but such a correlation could not be found.

When the change to arc melting was accomplished, there was an immediate improvement in the total impurity content, amount of segregated phases, and in hardness level. Carbon, oxide, and nitrogen contents were the most significant items lowered. In all respects this metal was equal to or superior to virgin Ames metal.

Attempts to correlate chemical composition with hardness values were somewhat more successful with arc-melted metal than with induction-melted metal, but not as good as would be desired. It did seem evident, however, that hardness increased with nitrogen content and decreased with higher aluminum content. Aluminum apparently acts as a scavenging agent for some of the nitrogen that is in solid solution and, for this reason, the limit for aluminum probably should be closer to 200 ppm or even 400 ppm. The maximum limit for aluminum should be no higher than one of these values, however, since low-melting eutectics would then be formed and would concentrate at grain boundaries. (3 w/o aluminum will result in a 100% eutectic structure of thorium and aluminum.)

The desired effect of low hardness obtained by limiting the carbon to 400 ppm and the nitrogen to 150 ppm in the chemical requirements is probably met in the arc-melted metal although the ratio of these two elements is different (generally 100-300 ppm of each). A limit of

200 ppm for each should be satisfactory.

It should be noted that the zinc content of the arc-melted metal is higher than that of the induction-melted metal from either Ames or FMPC. Thorium is apparently better freed from zinc during the relatively long induction melting cycle than during the very short time of melting when consumable electrodes are used. The larger amounts of zinc, however, do not seem to have any deleterious effect.

Calcium and magnesium contents were very low in all cases except for occasional ingots which were induction melted in top pour zirconia crucibles. The occasional high calcium content was undoubtedly due to residual calcium in the biscuit that distilled out during vacuum melting and condensed on the pouring lip of the crucible. When the molten metal was cast, some of this condensed "crud" was poured into the cast ingot.

Silica was also generally high in the induction-melted FMPC metal, originating from the silica contained in the zirconia crucibles.

The amounts of boron and cadmium in all types of metal were quite low. Ames personnel have emphasized, however, that boron content might be high if the hydrofluorination temperature were not high enough to form a volatile boron fluoride.

The rare earth contents specified in the desired chemical requirements were based on what their contents were thought to be in Ames thorium and on values recommended in 1950(14) for thorium use in the Materials Testing Reactor. It is questionable, however, whether it is economical to get the rare earth content down to such levels, although it probably should be lower than in the FMPC metal. For high burnup of thorium the question of the economics is less important. If irradiated virgin thorium is recycled, the importance of the original rare earth content is minimized, since the elements of very high cross section will be burned out during the first irradiation cycle.

INGOT QUALITY

Most of the information available on thorium ingot quality has been obtained from visual examination of as-cast and machined ingots and from examination of fabricated slugs. Successful radiography of ingots has not been possible due to the high density of the thorium. Also, nondestructive evaluation by ultrasonics has been hampered by the relatively large inclusion content of production metal.

Ames Metal

Two characteristics of Ames ingot quality stood out. First, the as-cast surfaces were generally covered with cold shuts necessitating the removal of approximately 1/4 inch of metal prior to fabrication.

Second, the interior of the ingots had considerable secondary pipe caused by metal shrinkage upon solidification.

Since the Ames as-cast ingots were only three and one-half inches in diameter, the metal yield was affected to an appreciable extent by machining to 3 to 3-1/4 inches. The poor surface quality of the ingots could probably have been improved, with correspondingly higher metal yield, by increasing the temperature of either or both the melt and the mold, but this would have been at the expense of crucible life and increased impurity pickup, that is, oxide from the beryllia crucible and carbon from the mold.

The extent of secondary pipe in the Ames ingots was a consequence of the large length-to-diameter ratio of the castings, 3-1/2 inches in diameter and 36 inches long. The reason for this shape, however, was the fact that it was designed for rolling to solid rod. Destructive examination of hot-rolled, 1.36-inch-diameter thorium slugs fabricated for Hanford showed some voids (as large as 1/8 inch along the slug axis) which were a result of the secondary pipe. A smaller length-to-diameter ratio for the cast ingots would have lessened the secondary pipe, but then the ingot shape would not have been suitable for rolling.

FMPC Induction-Melted Metal

The ingots cast at FMPC from the induction melting furnaces were 7 inches in diameter and weighed approximately 400 pounds, four times the weight of Ames castings. Preheated graphite molds were used; the surface quality was at times good but it was not reproducible. Normally up to one-third of the top end of the ingot had to be removed for the elimination of primary pipe. Before optimum casting conditions could be developed, the induction melting process was replaced by consumable electrode arc melting.

FMPC Arc-Melted Metal

In most respects the ingot quality of the 7-inch diameter, arc-melted ingots was considerably better than that of the induction-melted ingots either at Ames or FMPC. Surface quality was improved and cropping losses for removal of primary pipe normally were no more than 10% of each ingot.

There were, however, two types of ingot defects that resulted in approximately 12% rejection of production slugs prior to canning. These defects were characterized by fine cracks and "porosity" in extruded and machined slugs and were normally revealed only after the etching treatment required for canning. Although both types of defects were found in metal arc melted at the Bureau of Mines and at FMPC, the crack defect was more typical of the former and the "porosity" defect more typical of the latter. In the as-cast ingot these defects were generally found only after machining smooth and etching. The cracks in the Bureau of Mines ingots occurred primarily at the top end and were probably caused by the method of shutting off the arc at completion of melting.

The presence of cracks made forging very difficult. Normally, forging was not done, but when two experimental 10-inch-diameter ingots cast at the Bureau of Mines were forged down to a diameter of 7 inches the top ends split so badly that the final acceptable lengths of the forged pieces were no longer than the original 10-inch-diameter castings. During the forging operation the cracks at the top end had enlarged and had propagated over half the ingot length.

The "porosity" referred to above as being more typical of FMPC arc-melted metal was believed to be caused by segregated thorium oxide. During the slug etching process there was preferential attack at areas of segregated oxide with the result that pits or "porosity" developed. The reason for the greater frequency of this defect in FMPC arc-melted metal was that there was less surface scalping of the de-zinced derbies than at the Bureau of Mines.

FABRICATION OF THORIUM ELEMENTS

ELEMENT CORES

Rolling

Essentially all of the Ames metal used for radiation was hot rolled at Simonds Saw and Steel Co. at Lockport, New York. The billets (machined ingots) were heated to 1500°F and were rolled without difficulty from 3 to 3-1/4 inches in diameter down to approximately 1.4 inches in diameter without reheating. Heating was done in air and during the entire operation the oxidation losses totaled about 1/2 - 1%. Finishing temperatures were about 1000-1200°F. Rods were then straightened and machined to final dimensions.

When the FMPC pilot plant started up in 1954, rolling was contemplated as the means of fabricating ingots to slug form, the rolling to be done at Simonds Saw and Steel Co. Due to the mechanical properties of the metal, however, rolling did not prove to be satisfactory. At the first rolling attempt in September 1954, with approximately 10 ingots, only 1 ingot was reduced to rod form. Most of the others split during very early passes, some at even the first pass. By the fourth experimental rolling in early November 1954, quality of metal had improved so that 11 out of 12 rods were fabricated to 1-1/8-inch-diameter rods.

At the first large rolling (approximately 75 ingots), all the ingots were rolled to rod, but the best metal yield of acceptable slugs from any one ingot (uncropped and unconditioned weight of approximately

450 pounds) was only 32 slugs or 64 pounds, a yield of less than 15%.

Extrusion

Concurrently, with the earlier production rolling of Ames metal and later experimental rollings of FMPC metal, development work on different extrusion techniques was going on.

For the Ames metal there was no clear-cut advantage of any one fabrication process, but for the initial FMPC induction-melted metal, extrusion appeared to be a more suitable method.

Warm Extrusion

As an alternative for rolling as a fabrication method for Ames metal in the form of 3-inch-diameter billets, a process for extruding at temperatures somewhat below the hot working range was developed by the Brush Beryllium Corporation of Cleveland, Ohio.(15) With the equipment available at Brush, reductions were somewhat limited; in fact, a double extrusion was necessary for reducing a 3-inch-diameter billet to rod less than 1 inch in diameter. In this process the billet was coated with "Oildag" and heated to approximately 930°F. The ram, container, and die were heated to the same temperature. Although this process produced rod of the same quality as obtained by hot rolling, it was not considered as a serious candidate for production use.

Hot Extrusion

A small number of billets of larger diameter (approximately 5-1/2 inches) were cast at Ames for hot extrusion development and evaluation of the irradiation behavior of extruded thorium. These billets were successfully extruded at the Revere Copper and Brass Co., Detroit, Michigan (October 1952) with either a copper jacket or a salt lubricant. Extrusion ratios of approximately 40:1 were easily accomplished at temperatures of about 1200-1300°F with either lubricant, the extrusion pressure being about 10% higher when salt was used.

Prior to this time, some extrusion development on 2-inch-diameter billets in the temperature range of 1150-1500°F(16) using salt lubricants was done at Oak Ridge National Laboratory. The significant fact brought out there was that at the highest temperature the extrusion pressure was higher than at lower temperatures. Seizing or galling between the billet and container or dies was the apparent cause of this phenomenon since the pressure should decrease exponentially with increasing temperature.

During October 1954, Fernald metal of the same quality as used for the rollings described above was used for extrusion tests. In these tests six copper-clad billets, 6-1/2 inches in diameter, were extruded satisfactorily to 1-1/8-inch-diameter rods at Revere Copper and Brass Co.(17) Copper jacketing was employed because salt bath facilities were not available. During the following month, additional ingots were satisfactorily extruded at Adrian, Michigan, by the Bridgeport Brass Co.(18) These billets were heated in a salt bath with the adhering salt being used as a lubricant. It was evident from these tests that for this quality of metal, extrusion resulted in a considerably higher yield of metal.

When it was decided at the end of 1954 to change the melting procedure from induction heating to consumable electrode arc melting, it was also decided to extrude all thorium for production use. After the first three ingots that were arc melted at the Bureau of Mines were extruded on an experimental basis at Revere Copper and Brass in January 1955, all subsequent ingots that were melted at the Bureau of Mines and FMPC were extruded at Adrian on a semiproduction basis with full success. Extrusion temperatures were approximately 1350°F.

PROPERTIES OF FABRICATED ROD

The properties of fabricated rod depend on both the method of fabrication and the chemical purity of the thorium with its associated physical properties.

When rods were fabricated by either hot rolling or warm extrusion, the finishing temperatures were lower than for hot-extruded metal. In fact, the finishing temperatures of both hot-rolled and warm-extruded metal were below the hot working range and consequently the thorium was not recrystallized but partially cold worked with considerable residual stresses. In contrast, hot-extruded metal was completely recrystallized with a uniform fine grain structure.

In all methods of fabrication the secondary phases, particularly the oxide, were elongated in the direction of working. With high oxide content the resulting stringers were often continuous.

Except for the induction-melted metal from FMPC, essentially all rolled or extruded thorium was sound except for defects originating in as-cast ingots, as described earlier. The induction-melted FMPC metal had a tendency toward severe cracking during rolling.

Although both the FMPC induction-melted and arc-melted metal extruded satisfactorily to rod, there was a striking difference in metal quality shown by the behavior of each type of metal when etched in a hydrofluoric - nitric acid solution (as was necessary to prepare the surface for canning and to reveal cracks that were covered over with smeared metal by machining operations). The induction-melted metal normally pitted very badly whereas the arc-melted metal normally etched quite evenly. This behavior was attributed to the difference in the amount of segregated impurities.

A distinct difference between the induction-melted and arc-melted metal was also shown by a "squash" or compression test. Short sections of machined rod 1 inch in diameter and 1-1/2 inches long were compressed in the axial direction approximately 60%. Most of the induction-melted metal exhibited longitudinal surface cracks at this compression as a consequence of its greater level of segregated impurities, whereas the arc-melted metal performed quite well.

CANNING METHODS

Four aluminum canning or cladding methods were developed for the different elements required at Savannah River. These methods are:

1. Die sizing
2. Al-Si hot-dip canning
3. Hot-press canning
4. Coextrusion

Before discussing these canning methods, the various shapes and the reasons for using them will be described. The approximate dimensions of these shapes (without cladding) were as follows:

1. Unbonded slug, 0.808 inch in diameter and 10 inches long
2. Bonded slug, 1 inch in diameter and 6 inches long
3. Bonded slug, 1.68 inch in diameter and 7.2 inches long
4. Bonded tubular element, 2 inches in outside diameter and 12-1/2 feet long, with a 0.370-inch wall thickness

The first shape was developed for use in control rods. For this use the aluminum-canned unbonded slugs had to be sheathed in a long aluminum tube (14 feet) that was swaged over the canned slugs and then welded at each end with appropriate end fittings. Helium gas filled the gap between the can and tube. This method of sheathing permitted double protection against failure by water corrosion and was considered adequate. All other shapes were only singly canned, and a bonded system was considered to be necessary because of the difference in corrosion behavior of bonded and unbonded elements (discussed on page 8 of this report).

The second shape was developed for use with enriched uranium-aluminum alloy fuel slugs of the same diameter (1 inch). These fuel slugs were alternated with thorium slugs in the same water channel of the reactor.

The third and fourth shapes were developed for use with enriched uranium-aluminum alloy fuel tubes. Either the thorium slugs, 1.68 inches in diameter, or the thorium tubes were to be irradiated inside of these fuel tubes.

Only a brief description of each of the methods of canning will be given here.

DIE SIZING

The method of die sizing had previously been used at Hanford. In this method a bare slug is placed in an aluminum can and an aluminum cap is placed on top of the slug. The assembly is then pushed through a die by means of a mandrel which exerts pressure on the cap. Dimensions of the die and components are adjusted so that there is some reduction in the thickness of the can wall. The resulting gap between the can and slug is less than one mil. After sizing, the excess can length is machined off and the interface between the can wall and cap is welded.

Al-Si CANNING

A technique for obtaining bonded slugs was developed by the Savannah River Laboratory(19) and is a modification of the standard triple-dip process for natural uranium slugs. However, graphite sleeves are used in place of the steel sleeves normally employed for uranium slugs, since the coefficient of thermal expansion of thorium is considerably less than that of uranium, and upon cooling the thorium slug does not shrink away from a steel sleeve sufficiently for easy removal.

HOT-PRESS CANNING

Procedures for canning thorium slugs by hot pressing were developed for du Pont by the Sylvania Electric Products Co.(20) A slug and aluminum cap are inserted into an aluminum can and the assembly is heated in an inert atmosphere to 530-550°C. The assembly is then pressed in a one-piece die in vacuum by means of two mandrels, one acting on each end of the assembly at a pressure of approximately 30,000 psi for 10 minutes. The pressing is done with the can in an inverted position so that prior to pressing there is a gap of about 1/4 inch between the end of the slug and the bottom of the can. This space permits a sliding action between the core and can at the start of the pressing operation and results in a more uniform bond layer. After hot pressing, the flash is trimmed off and the interface between the can and cap is welded at Savannah River. The primary purpose of this weld is to test the quality of the bond. If the bond is not satisfactory, a bad weld results.

Hot pressing in this manner results in an intermetallic bonding layer approximately 0.2 mil thick with a bond strength of 16,000 psi. High bond strength is obtained only when the bonding layer is very thin since thorium-aluminum intermetallic compounds are very brittle. In the Al-Si canning process, the intermetallic bonding layer is 5 to 10 times thicker than that obtained with hot pressing and the resulting bond strength is considerably weaker.

Certain metal quality requirements are of great importance in the hot-press canning method. First, the hardness level of the slugs should be kept as uniform as possible; slugs of varying hardness can be canned satisfactorily, but with varying hardness the hot-pressing conditions have to be varied accordingly. Although the preferred maximum hardness is BHN 60 (500-kg load), slugs with hardness of BHN 70 have been canned satisfactorily. Second, aside from the undesirable effects that may occur during irradiation, cracks in the slugs that extend to the surface and pits that develop during etching as a result of segregated oxide may retain etching solutions which later cause difficulties in either canning or irradiation.

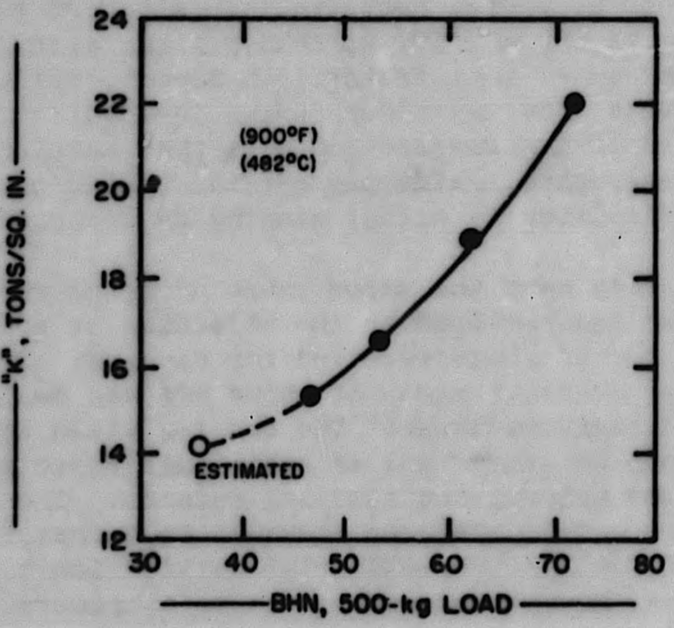
Such cracks and pits were the major cause of metal rejection prior to hot-press canning and resulted in the rejection of approximately 12% of the total number of slugs received for canning. Even with this rejection rate an over-all yield of about 80% was realized, from as-received to irradiated slugs. The canning yield at Sylvania was actually about 99% but there was an additional rejection of 8% at Savannah River for welding and handling defects. The slugs rejected at Savannah River could have been recanned satisfactorily and this would have increased the over-all metal utilization to about 88%. This was not done, however, because of time considerations.

One unexpected advantage of hot pressing over Al-Si canning was that, after canning, the thorium core had residual compressive stresses on the surface and tensile stresses along the axis which tended to minimize the heat flux stresses during irradiation.

COEXTRUSION OF TUBULAR ELEMENTS

The optimum design of a thorium target for the Savannah River reactors is considered to be a tubular design. The most practical way to clad this type of element was considered to be coextrusion, although it was recognized that this was much more difficult than the coextrusion of aluminum cladding over an aluminum alloy core, because of the greater difference in physical properties between thorium and aluminum. Nuclear Metals, Inc., had developed this method for cladding uranium-aluminum alloy tubes with aluminum and agreed to determine its feasibility with a thorium core.(21) In this process a composite extrusion billet is prepared consisting of a thick-walled tubular core, aluminum alloy end plugs of the same diameters, and inner and outer aluminum sheaths. The end plugs are welded to the sheaths and the billet is evacuated and sealed off. The billet is then heated, lubricated, and extruded through a streamline flow die. To minimize the length of the normal extrusion defects at each end of the core, the core and end plugs are machined to appropriate matching shapes before billet assembly.

For the thorium coextrusion to work successfully, the metal must have the low hardness that is characteristic of good quality thorium with a relatively low impurity content. Actually, it is the extrusion constant of the thorium at the extrusion temperature that is important, but this is directly related to the hardness at room temperature as shown in the figure.



EXTRUSION CONSTANT K VS. HARDNESS

The data were obtained by Nuclear Metals, Inc. The preliminary specification for hardness was set at a maximum of BHN 60, but it developed that an ingot hardness of BHN 55 (500-kg load) was required for satisfactory coextrusion.

The next most important requirement for satisfactory coextrusion is fine grain size. Arc-melted ingots from the Bureau of Mines had excessively large grain size and this resulted in a corrugated interface between the thorium and aluminum cladding. Pre-extrusion or forging of Bureau of Mines arc-melted ingots reduced the grain size to satisfactory levels. FMPC arc-melted ingots had a finer as-cast grain size than Bureau of Mines metal and this was believed to be due to the greater flow of water in the copper molds used at FMPC with the result that the solidification rate was more rapid. This made it unnecessary to refine the grain size of the FMPC metal.

For any coextrusion, the end plug material must have about the same stiffness as the core material at the extrusion temperature. With a thorium core, a 6 w/o magnesium-aluminum alloy was the most suitable material developed.

IRRADIATION OF THORIUM AND REACTOR PERFORMANCE

Compared with uranium, thorium metal has shown remarkable stability upon irradiation. Volume or density changes have been negligible despite the use of varying types of metal, fabrication history, and canning methods. The data in the following table show actual changes in dimensions of thorium production-type elements of different sizes and shapes. These changes are actually little more than the dimensional accuracy.

Dimensional Stability of Thorium Elements*

	Dimensions	Maximum Change in Length, mils	Maximum Change in Diameter, mils	Maximum Warp, mils
Slug(1)	0.808" Dia. x 10" long	-9 to +11	-2 to +2	0 to +3
Slug(2)	1" Dia. x 6" long	-7 to +6	-2 to +6	-1 to +6
Slug(3)	1.36" Dia. x 6" long		-11 to +3	
Tube(4)	2" OD x 2' long	-10 mils (Avg.)	+2 mils (Avg.)	No visual warp

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* Measurements made on aluminum cladding

(1) Extruded Ames metal - SRP shape irradiated at Hanford - unbonded

(2) Arc-melted FMPC metal - SRP shape irradiated at Savannah River - bonded

(3) Hot-rolled Ames metal - HAPO shape irradiated at MTR - unbonded

(4) Coextruded, arc-melted FMPC metal - prototype SRP shape irradiated at MTR - bonded

Exposure of the SRP type elements ranged up to 3000 g/t whereas the HAPO slugs irradiated in the MTR had total atom burnouts up to approximately 10,000 g/t.

Data on small size experimental specimens confirm the order of magnitude of these changes. The greatest change in density measured on any thorium metal as a result of irradiation was on a 5.5 w/o U^{235} - thorium alloy specimen 1/4" x 1" x 0.032", that was exposed to a total atom burnout of 1.4%. The density change in this case was 1.44%.

Actually, the small changes in volume of the metal which take place during irradiation can be rationalized on the basis of the total volume of products formed relative to the original volume of the thorium. In the case of uranium, Weber and Howe,(22) at Knolls Atomic Power Laboratory, have calculated that the integrated gram-atom volume of fission products, based on the atomic volumes of individual atoms, should be four times the volume of the gram-atoms of uranium fissioned. This should result in a volume growth of 3% for a burnout of every 1% of the total number of uranium atoms. Within experimental accuracy this figure has been confirmed for irradiation of uranium as long as the irradiation temperature is less than that at which fission gas swelling begins to occur.

Because of the considerably lower density of thorium, fission products have a lesser effect on volume changes. For instance, if one cc of thorium were to be completely converted to U^{233}, a volume of only 0.615 cc of uranium would result. It would then require a fission burnout of the resulting U^{233} of approximately 25% for the larger fission product to compensate exactly for the volume decrease in going from thorium to uranium. Further, if it were considered that thorium went directly to fission products, then the volume increase would be only 1% for every 1% of the thorium atoms burned out compared with the 3% volume increase for uranium. Thus, for a one-inch-diameter slug irradiated long enough for 1% of the original thorium atoms to be converted to fission products, the net change in diameter would, on this basis, be only five mils, and it would be this large only if the entire volume increase were in the diametral direction.

In addition to density changes, dimensional stability of uranium is characterized by dimensional changes resulting from its anisotropic properties. For instance, single crystals of uranium increase in length in one axial direction, contract in another and remain the same in the third. Also, when uranium is irradiated after rolling in the alpha range without further heat treatment, it generally grows in the direction of fabrication due to preferred orientation effects. Thorium, on the other hand, is cubic in structure and is isotropic in all these dimensional aspects.

Other property changes of interest are hardness and ductility. Unfortunately, preirradiation hardness measurements were not taken on most of the metal specimens for which postirradiation measurements at Savannah River are available.

From Hanford and Oak Ridge data, however, it appears that the hardness increase for thorium irradiated to moderate burnouts, up to 2000 g/t, is quite small, on the order of 10-20 points on the Rockwell "B" scale.

KAPL believes that at least some of the hardening effect during irradiation is caused by an aging phenomenon.(23)

Hanford also made some ductility measurements on full-size thorium slugs after irradiation exposures up to 2000 g/t. It was found that six-inch-long slugs could be bent approximately 90° without fracture. This is at least an order of magnitude greater than can be obtained with uranium.

Although the reactor performance of thorium with respect to dimensional stability has been excellent, the behavior of three irradiation failures of unbonded thorium elements at Hanford[24] has not been so good. Two significant observations characterize these failures; first there was considerable swelling and splitting of the aluminum jacket over large areas caused by the formation of corrosion products and, second, splitting of the thorium core. One of the failed slugs was stuck so badly in its process tube that the entire tube had to be removed from the reactor. In another failed slug the core actually fell apart into several pieces after the aluminum can had been stripped off. Hanford personnel believe that each failure was caused by water entry through a defect in the weld between the can and end cap allowing corrosion of the core to take place. When corrosion of the core started, it continued not only on the surface but it penetrated along metal defects and/or segregated impurities. Since this was Ames thorium, the primary segregated impurity would be thorium oxide. On the other hand, the splits in the core were filled with only relatively small amounts of corrosion products and this leads to the speculation that the core may have split, during irradiation, from internal causes and that this then was the primary cause of water entry. If this were the case, the segregated impurities undoubtedly acted as stress risers since the normal thermal stresses are considered insufficient to cause splitting.

Nothing can be said of the behavior of failed thorium elements that have been bonded, since there have been no recorded failures with bonded elements. On the basis of out-of-pile corrosion tests, it is expected that the effects of corrosion through a cladding defect would be much less serious.

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