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VACUUM INDUCTION MELTING AND CASTING OF THORIUM AND THORIUM-URANIUM ALLOYS

AEC Research and Development Report

ATOMICS INTERNATIONAL
A DIVISION OF NORTH AMERICAN AVIATION, INC.

Price $.50
Available from the Office of Technical Services
Department of Commerce
Washington 25, D. C.

NAA-SR-5833
METALLURGY AND CERAMICS
25 PAGES

VACUUM INDUCTION MELTING AND CASTING OF THORIUM AND THORIUM-URANIUM ALLOYS

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A DIVISION OF NORTH AMERICAN AVIATION, INC.
P.O. BOX 309 CANOGA PARK, CALIFORNIA

CONTRACT: AT(11-1)-GEN-8
ISSUED: OCT 30 1961

DISTRIBUTION

This report has been distributed according to the category "Metallurgy and Ceramics" as given in "Standard Distribution Lists for Unclassified Scientific and Technical Reports" TID-4500 (15th Ed.), August 1, 1959. A total of 600 copies was printed.

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ABSTRACT

Refractory-oxide-coated graphite was investigated as a crucible material for producing Th-U castings. Oxides of Y, Th, Zr, and Be were applied to graphite crucibles by wash-coating and, when possible, by flame-spraying. Thorium as well as alloys of Th 1 to 13 w/o U were prepared by vacuum induction casting. The castings were evaluated on the basis of number and intensity of surface and internal defects, homogeneity of composition, and metallurgical properties. Effectiveness of the refractory oxide coating was measured in terms of crucible attack and degree of carbon contamination in the Th-U castings. Best results were obtained with wash-coatings of Y_2O_3 and ZrO_2 and a flame-sprayed coating of ZrO_2. ThO_2 was found to be unsuitable and BeO requires additional investigation.

I. INTRODUCTION

The use of thorium-uranium alloys as reactor fuel material is dependent in part on the economics of fuel element fabrication. Th-U fuels have been considered for use in four power-reactor concepts, namely, SCR (Sodium Cooled Reactor), AETR (Advanced Epithermal Thorium Reactor), CETR (Consolidated Edison Thorium Reactor), and ERNR (Elk River Nuclear Reactor). A Th - 7.6 w/o U alloy has been in use as the second core in the SRE since the fall of 1960. This fuel was made by extrusion, followed by cold swaging.[1]

The objective of the present project was to develop a low cost fabrication process for producing sound Th-U castings in any desired shape and quantity.

Previous efforts by other laboratories engaged in the induction melting of Th and Th alloys were directed towards the use of crucibles made of BeO and stabilized ZrO_2.[2,3] The high cost of fabricating these crucibles, their short life, and the severe toxicity problem with BeO precluded the use of such crucibles in a low cost fabrication process. Graphite is an ideal crucible material with regard to low cost, high strength, abundance, and ease of fabrication. However, it is readily attacked by molten Th and Th-U alloys. Molten Th wets graphite to the extent that it will creep up along the walls of a crucible and stopper rod. The dissolved carbon raises the melting point. Solidification then causes bridging, which often prevents casting. Under these conditions, the Th-U alloys will be contaminated with up to one percent of carbon. An experimental program to develop a suitable coating to prevent attack of graphite was undertaken.

II. EXPERIMENTAL

A. PROTECTIVE COATINGS FOR GRAPHITE CRUCIBLES

To prevent attack of the graphite, refractory oxide coatings were applied by painting (wash-coat), or flame-spraying, using both oxy-acetylene and plasma-jet torches. Four oxides were selected for study on the basis of (a) chemical inertness determined from their respective heats of formation (ΔH) as listed in Table I, (b) microscopic thermal neutron cross-section, (c) melting point, and (d) compatibility with carbon at reduced pressures.

TABLE I

HEATS OF FORMATION FOR REFRACTORY OXIDES

Oxide	ΔH_{298}(4) (kcal/g atom O_2)	Melting Point (°C) (5)
Y_2O_3	-450	2410
ThO_2	-310	3300
ZrO_2	-260	2677
BeO	-147	2550

A desired property of a protective coating on a graphite crucible or mold is that it undergo no decomposition reaction, and no reaction with either the graphite or the molten metal. The attendant negative free-energy change ($-\Delta F_t = -\Delta H_t + T\Delta S_t$, where ΔH is the enthalpy change, and ΔS the entropy change, evaluated at temperature) is a criterion for estimating the tendency of such reactions to occur. However, accurate calculation of free energies is complex because of the elevated temperatures and low pressures prevailing during the melting and casting process, and because of the possible formation of solutions. As a very rough guide in estimating inertness of the refractory oxides that were tested as coatings, the heat of formation from the elements at 298°K ($-\Delta H_{298}$) was used. On this basis, the oxide which appears most inert with a melting point greater than 2400°C, was Y_2O_3. Three other oxides, ThO_2, stabilized ZrO_2, and BeO, were also evaluated as protective coatings for graphite.

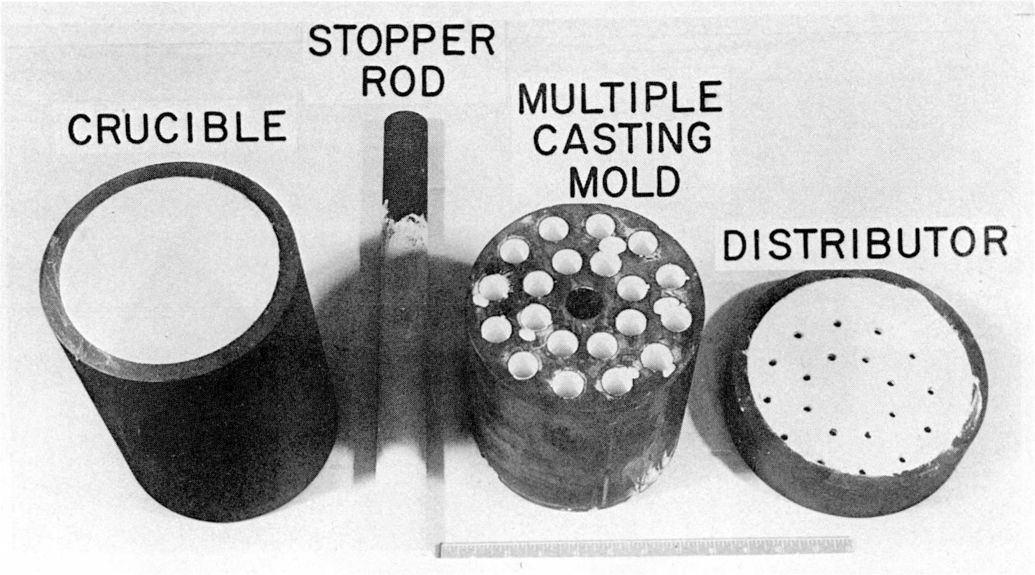
The oxides were used predominately as a wash coat. Only ZrO_2 (stabilized with CaO) was flame-sprayed. Y_2O_3 could not be sprayed because the required mesh size of -100 +325 was not commercially available at the time of this experimental work. (However, it was subsequently obtained and success has been attained in spraying with the plasma torch.) BeO and ThO_2 were not sprayed due to the lack of a suitable enclosure for spraying toxic and radioactive materials. Coatings applied as a wash averaged 0.015 in. thick compared with stabilized ZrO_2 spray coatings which averaged 0.010 in. The graphite used was the ATJ-grade of the National Carbon Company. Surfaces of crucibles, molds, and other components which normally came in contact with molten metal were first cleaned with an abrasive and a volatile solvent, and then painted with a refractory oxide slurry composed of 50/50 w/o ratio of oxide to binder. A binder found to be suitable was an acrylic lacquer. The coating was allowed to air-dry and was then oven-dried at 500°F for two hours to remove residual moisture. Graphite components wash-coated and flame-sprayed are shown in Figure 1.

B. MELTING AND CASTING

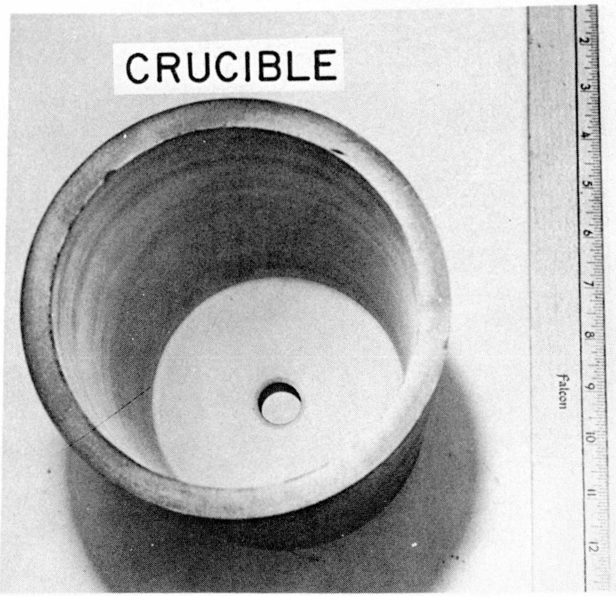
Melting and casting was performed in a 100-kw vacuum induction furnace. The average charge, which weighed 5 kgs, was melted in a bottom-pour, graphite crucible 4-5/8-in. ID (1/2-in. wall) x 9 in. deep. In addition to melting pure Th, alloys prepared included Th + 1, 5, 7.6, and 13 w/o U. The casting furnace was evacuated to 100 microns (Hg) or less at room temperature. The charge was heated to 1400°C at a rate of 50°C/min. Power input from the motor-generator source was approximately 35 kw. At 1400°C, the power input was reduced to 20 kw and the charge allowed to outgas until an equilibrium vacuum of less than 100 microns (Hg) was obtained. Power input was then increased to 40 kw and the charge heated to the desired pouring temperature, which was between 1750° and 1850°C. The molten charge was allowed to remain in contact with the crucible from 4 to 12 minutes before being poured into coated graphite molds. Pouring was achieved by lifting a graphite stopper-rod away from the pour hole at the base of the crucible.

C. RADIOGRAPHIC INSPECTION

All castings were radiographically examined for internal defects, using a Cobalt-60 source.



a. Wash Coated with Y_2O_3



b. Flame Sprayed with Stabilized ZrO_2

Figure 1. Graphite Components

D. CHEMICAL ANALYSIS

Carbon was determined conductiometrically. The procedure consisted of complete combustion of C in the sample to CO_2, which was subsequently dissolved in a $BaSO_4$ solution. The change in electrical conductivity of the solution indicated the amount of carbon present. Impurities were determined by emission spectrography; oxygen and hydrogen by vacuum fusion; and nitrogen by the Kjeldahl method.

E. METALLOGRAPHY

Metallographic samples of the Th and Th-U alloys were prepared by electrolytic etching. The etchant used was 5 volume percent HNO_3 in glycerine. A current density of 1/2 amp/cm^2 was used for 15 seconds. Following etching, the samples were rinsed in glycerine-ethyl alcohol solution. This method was satisfactory, even though some selective pitting was evident.

III. DISCUSSION OF RESULTS

A. CASTING

The casting process was evaluated on the basis of producing sound castings with a minimum of carbon contamination. Thorium and thorium-uranium alloys were successfully cast to dimensions in the range 3/8- to 3-in. diameter by 6 to 12 in. long. Figures 2, 3, and 4 are representative of the castings made in this investigation. Castings in the range of 1-1/2 to 3 in. diameter were sound internally except for centerline shrinkage starting at the top and extending to a depth of 1/2 to 2 in. Castings less than 1-1/2 in. diameter contained no appreciable centerline shrinkage, but did occasionally exhibit random porosity and cold shuts. This was particularly true for 3/8-in. diameter castings of Th and Th-1 w/o U, but rarely occurred in Th-5 to 13 w/o U alloys. The shrinkage in the larger castings was principally due to an inadequate riser which varied with the amount of skull remaining in the crucible. At equal pouring temperatures, the Th-U alloys had better castability than Th. This was expected in view of the decrease in the liquidus-solidus temperature with increasing U, as shown in the Th-U phase diagram.[6]

B. CRUCIBLE EROSION

The degree of graphite attack was estimated visually, and then measured more accurately by carbon analysis of the resultant castings. Figures 5 and 6 show the extent of crucible erosion for the various refractory oxide coatings used.

C. CARBON CONTAMINATION

Carbon contamination was found to be a function of:

1) refractory oxide coating and the method of application,

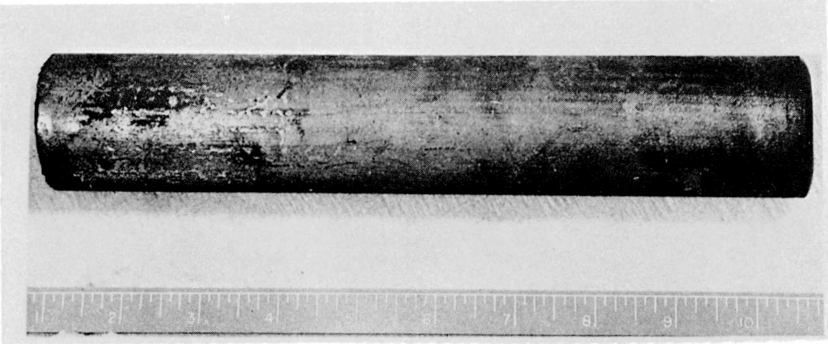
2) molten time (total time between melting and pouring of an alloy),

3) pouring temperature, and

4) w/o U in Th.

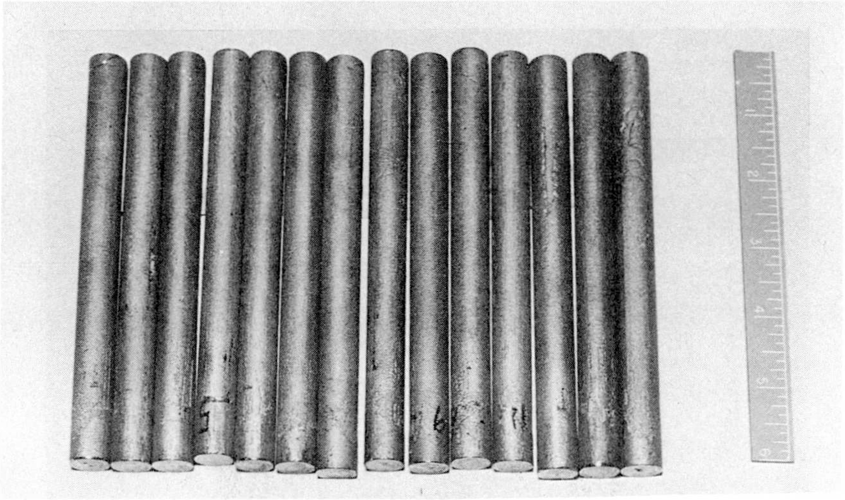
Table II gives a comparison of the carbon contamination in Th metal with the protective oxide coating used at a pouring temperature of 1830°C and a molten time of seven minutes.

a. ThO_2 Wash Coat

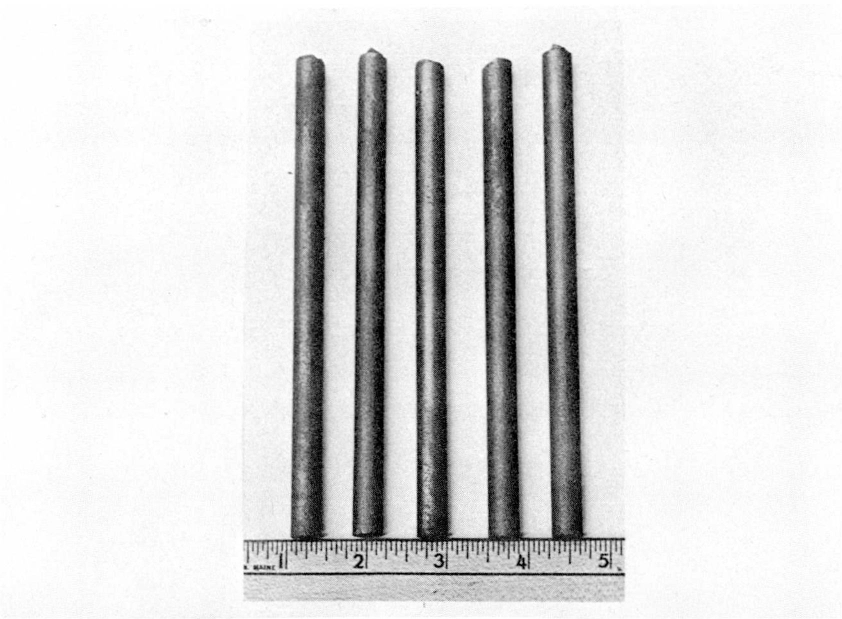


b. Y_2O_3 Wash Coat

Figure 2. As-Cast Thorium Ingots, Melted in Wash-Coated Graphite Crucibles



a. Th-1 wt % U



b. Th-13 wt % U

Figure 3. As-Cast Th-U Alloy Slugs, Meltedin Wash-Coated Graphite Crucibles

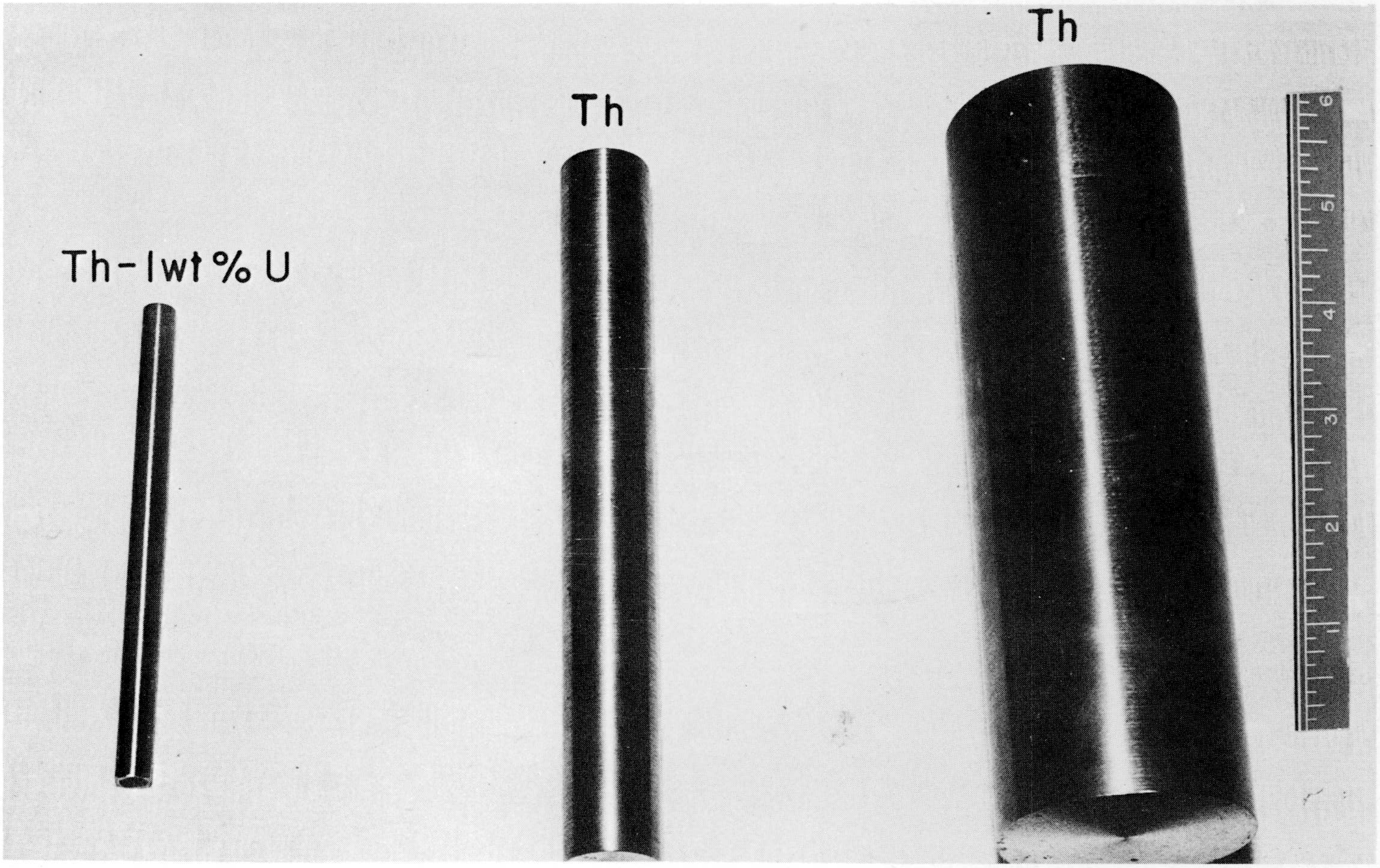
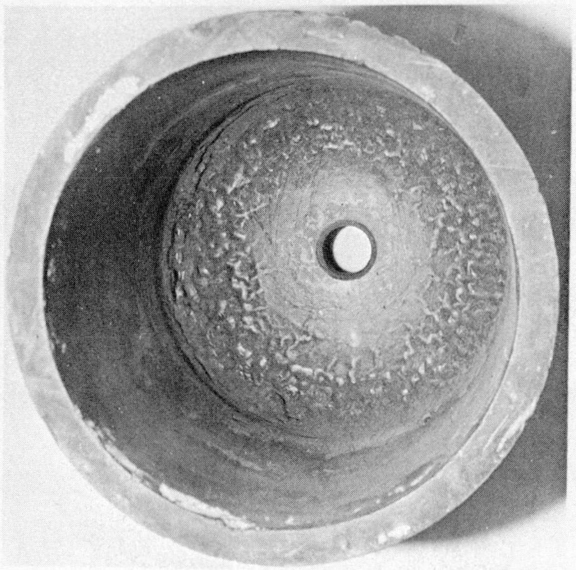


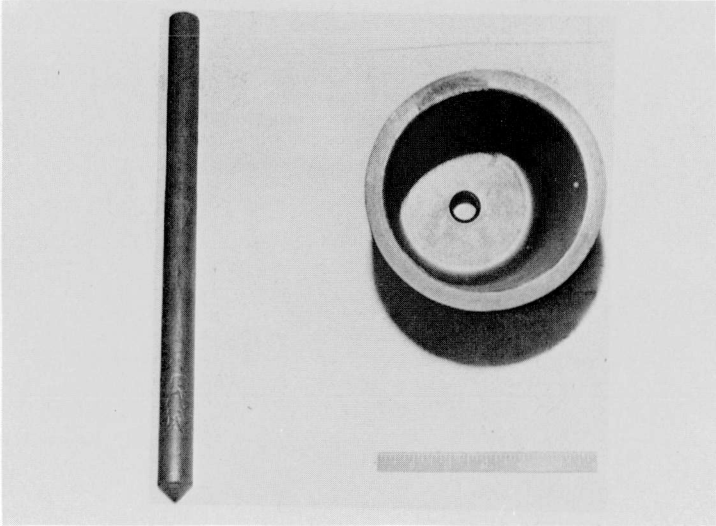
Figure 4. As-Machined Slugs of Th and Th-U Alloy



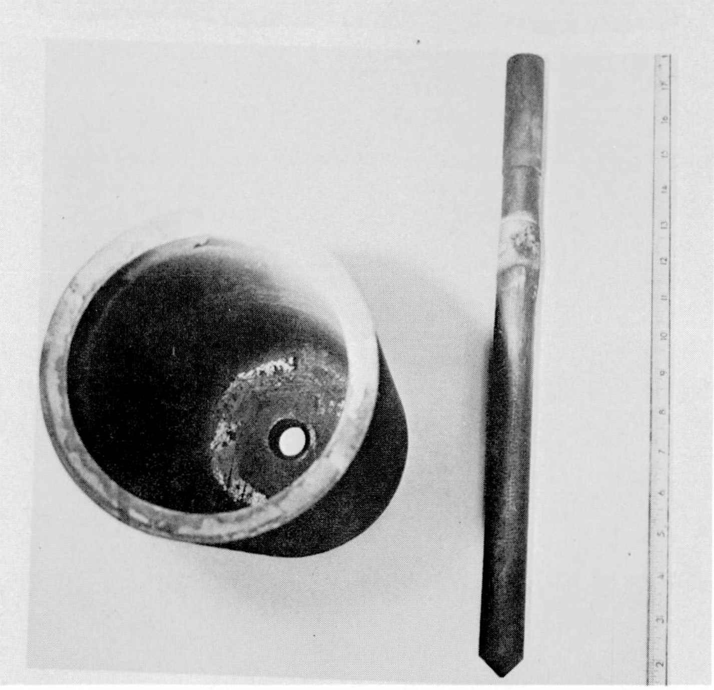
a. ThO_2 Wash Coat
(Severe Graphite Attack. Deep
Channels at Base and Adjacent
Wall)

b. ZrO_2 Wash Coat, Stabilized with 15 wt % Y_2O_3
(Some Erosion Observed Along Wall,
Adjacent to Base)

Figure 5. Condition of Wash-Coated Graphite
Crucibles After Melting Thorium



b. Stabilized ZrO_2 Spray Coat
After Melting Th - 1 wt % U



a. Y_2O_3 Wash Coat - After Melting Th
(Slight Erosion on Stopper-Rod)

Figure 6. Condition of Graphite Crucibles and Stopper-Rods

TABLE II

CARBON CONTAMINATION OF THORIUM AS A FUNCTION OF CRUCIBLE COATING

Oxide	Method of Application	Coating Thickness (in.)	Carbon Pickup (ppm)
ThO_2	Wash	0.015	7700
BeO_2	Wash	0.015	1700
Y_2O_3	Wash	0.015	450
ZrO_2 + 15% Y_2O_3	Wash	0.015	500
ZrO_2 + 5% CaO	Flame-Spray	0.015	400

The high pickup experienced with ThO_2 coatings is attributed to its poor thermal shock resistance, which results in spalling and flaking, leaving areas of graphite exposed to molten Th. Although BeO is included in the comparison, the data shown are based upon a limited effort due to the toxicity problem. At Fernald, the National Lead Company used a BeO wash on graphite for induction-melting of Th. This reportedly produced the least carbon contamination.[7] On the other hand, the Davison Chemical Company, after using BeO wash on graphite for casting 100-kg Th ingots, reports carbon contents as high as 1800 ppm. These ingots were subsequently hot-forged and cold-rolled into 1/2 in.-thick plates for the AETR critical experiment.[8]

Y_2O_3 and ZrO_2 washes afforded good protection. A flame-sprayed coating of ZrO_2 allowed the least carbon pickup.

The effect of molten time and pouring temperature on carbon pickup, using a Y_2O_3 wash coat on graphite, was determined for a Th-13 w/o U alloy held for molten times of 4 and 7 minutes respectively and poured at various temperatures between 1780° and 1850°C. The effect of w/o U in Th was also determined at a constant pouring temperature of 1800°C. Results are expressed graphically in Figure 7. The increase in carbon pickup with increasing U content is attributed to an increased tendency for highly superheated U to react with the protective oxide coating and graphite. In addition, there is a decrease in the melting range of the Th-U alloy which gives it a greater fluidity and wetting action.

D. IMPURITIES OTHER THAN CARBON

Interstitial impurities, i.e. oxygen, hydrogen, and nitrogen, were determined for Th melted in a Y_2O_3-coated crucible. Results are listed below and

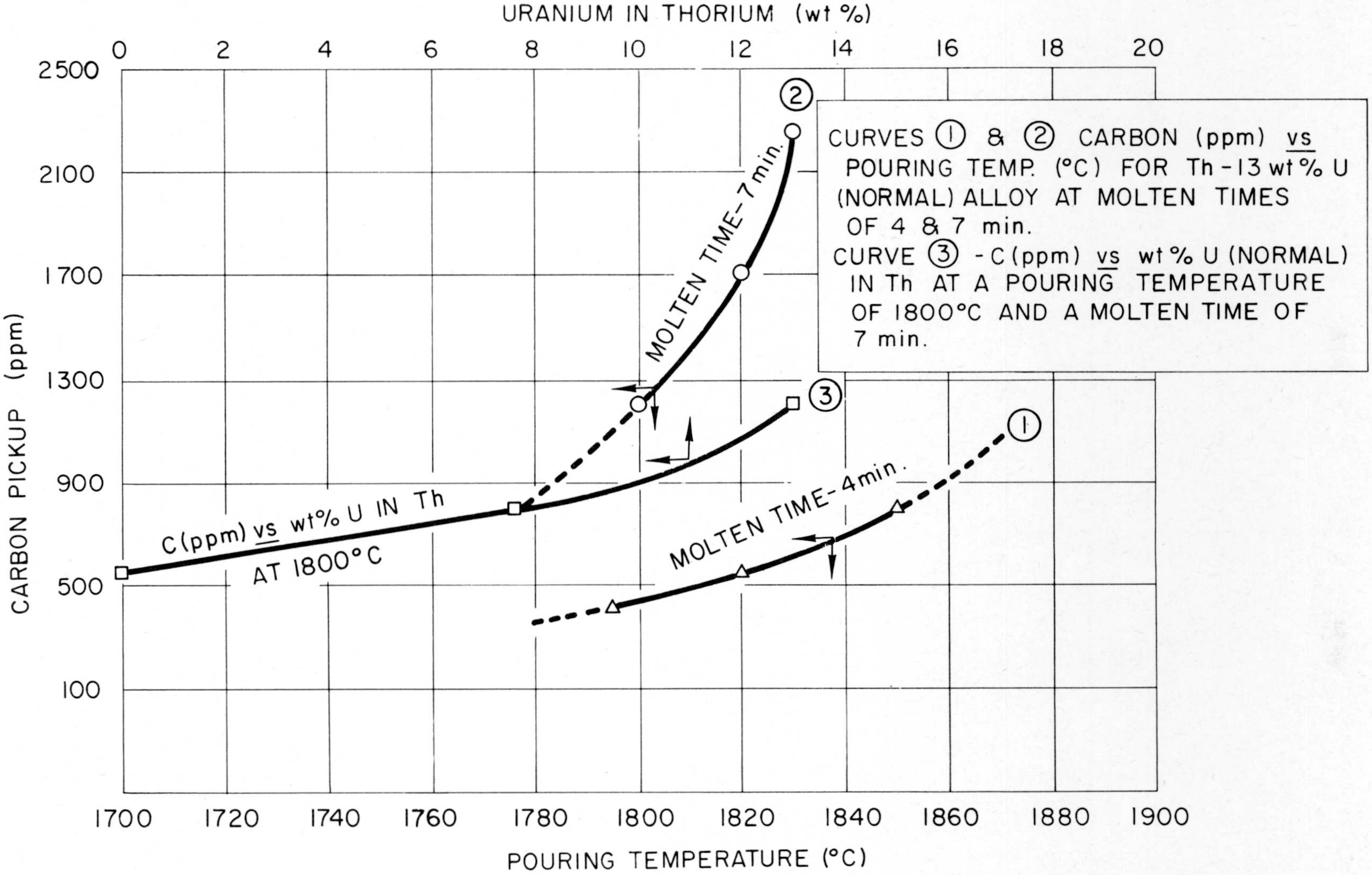


Figure 7. Effect of Molten Time, Pouring Temperature, and Weight Percent of U in Th on Graphite Crucible Erosion

are compared with the impurities in the original Th derby. Molten time for this heat was 4 minutes and pouring temperature was 1800°C.

TABLE III

INTERSTITIAL IMPURITIES IN MELTED THORIUM USING YTTRIA

(ppm)

Sample	O_2	H_2	N_2
Th derby metal	1720	30	100
After induction-melting in Y_2O_3-coated graphite	1900	20	100

A further evaluation of the stability of the refractory oxide coatings used was made by comparing the oxygen content in Th castings. These data are presented in Table IV. The oxygen content in the Th derby metal is taken as the control.

TABLE IV

OXYGEN IN THORIUM <u>VS</u> REFRACTORY OXIDE COATING

Coating	Method of Application	O_2 (ppm)
Th derby	-	1720
BeO	Wash	1850
ThO_2	Wash	4000
Y_2O_3	Wash	1900
ZrO_2 + 15% Y_2O_3	Wash	2300

Spectrographic analyses of the Th derby and Th melted in coated graphite crucibles are given in Table V.

E. HARDNESS

Room-temperature Rockwell "A" hardness measurements were obtained on the as-cast Th and Th-U alloys. Figure 8 shows the effect of carbon content on hardness of Th and Th-1 to 13 w/o U. Hardness appears to be significantly increased with both increasing carbon and uranium contents, the former producing the greater effect. Values shown are averages of five or more impressions.

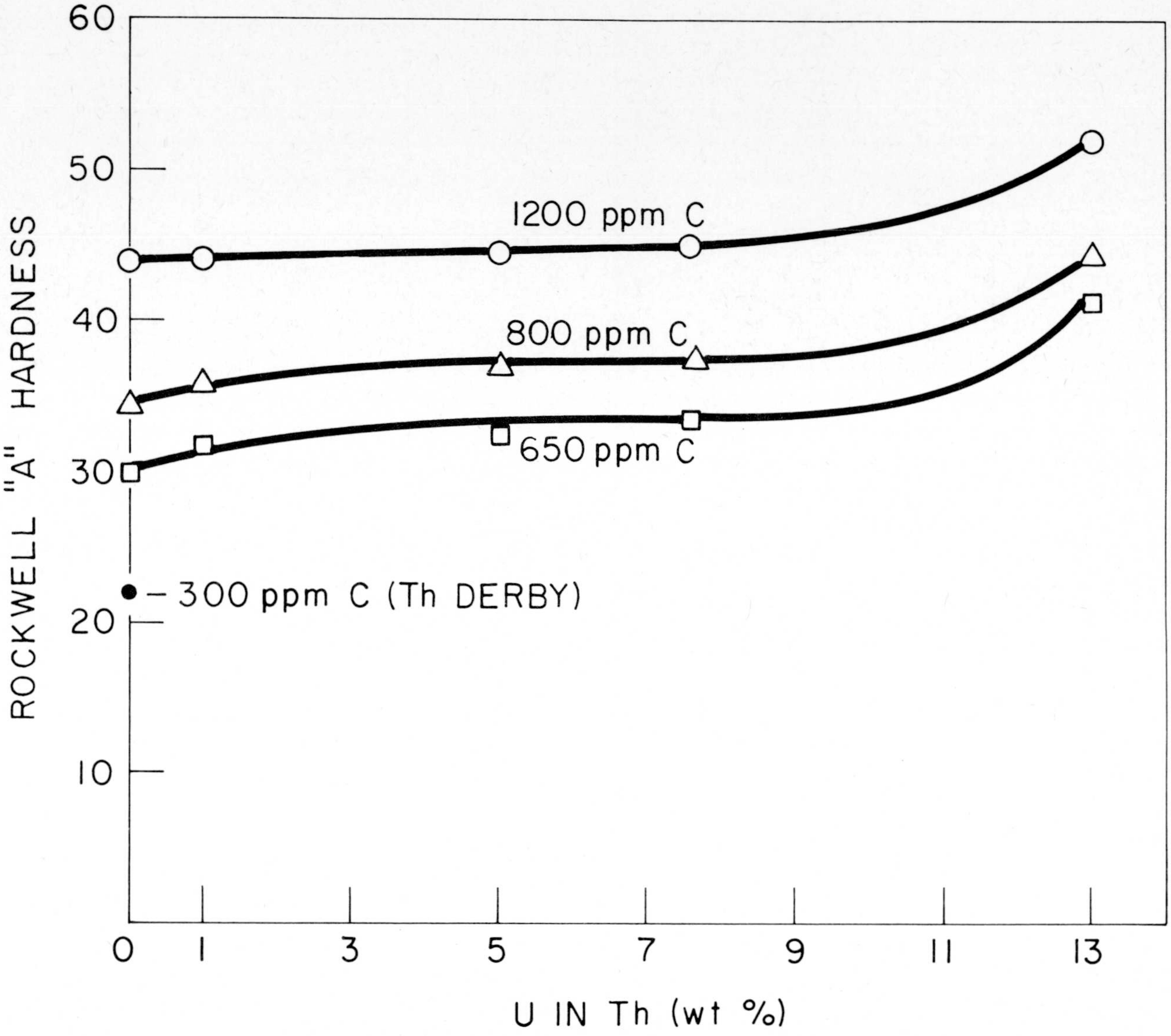


Figure 8. Effect of Carbon and Uranium on Hardness of As-Cast Th and Th-U Alloys

TABLE V

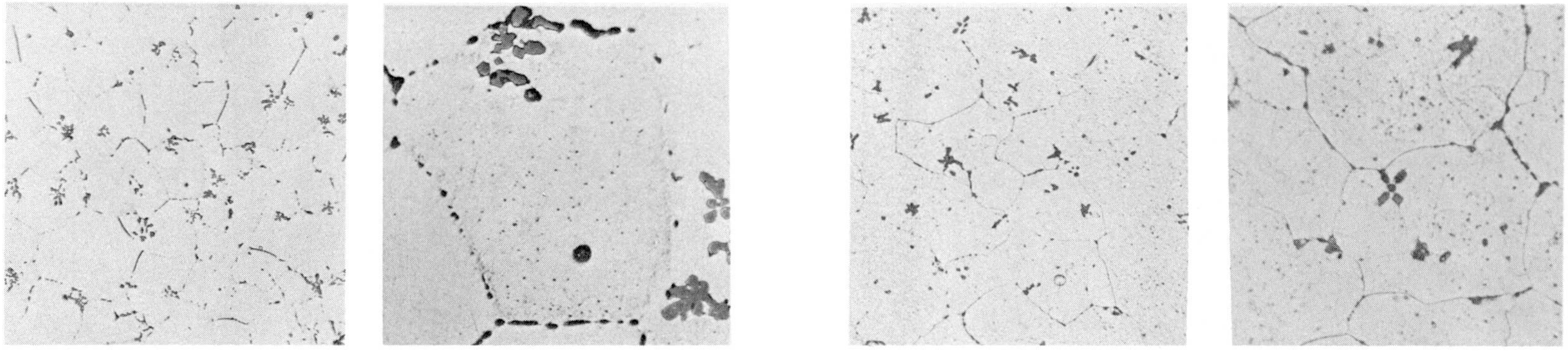
SPECTROGRAPHIC ANALYSES OF MELTED THORIUM
(ppm)

Element	Th Derby	In ThO$_2$-Coated Graphite	In BeO-Coated Graphite	In ZrO$_2$-Coated Graphite	In Y$_2$O$_3$-Coated Graphite
Ag	< 1	< 1	0.2	0.2	< 1
Al	10	85	20	75	15
Be	5	8	>200	20	< 10
B	< 1	< 2	6	6	6
Cd	< 1	< 1	> 0.5	< 0.5	< 0.5
Ca	5	15	20	20	15
Co	1	< 2	< 1	1	1
Cr	10	40	100	100	15
Cu	45	35	20	25	20
Fe	60	>200	200	150	150
Mg	< 1	< 1	1	< 1	< 1
Mn	3	3	5	< 5	< 5
Mo	10	25	20	20	15
Na	< 5	< 5	< 10	< 10	< 10
Ni	5	< 1	40	40	20
Pb	2	2	10	10	2
Si	12	20	15	15	10
Sn	1	1	1	1	1
V	5	22	< 10	< 10	< 10
Y	< 1	< 1	< 1	< 1	75
Zn	<10	< 10	20	20	10
Zr	< 5	< 10	< 10	>200	< 10

F. MICROSTRUCTURE

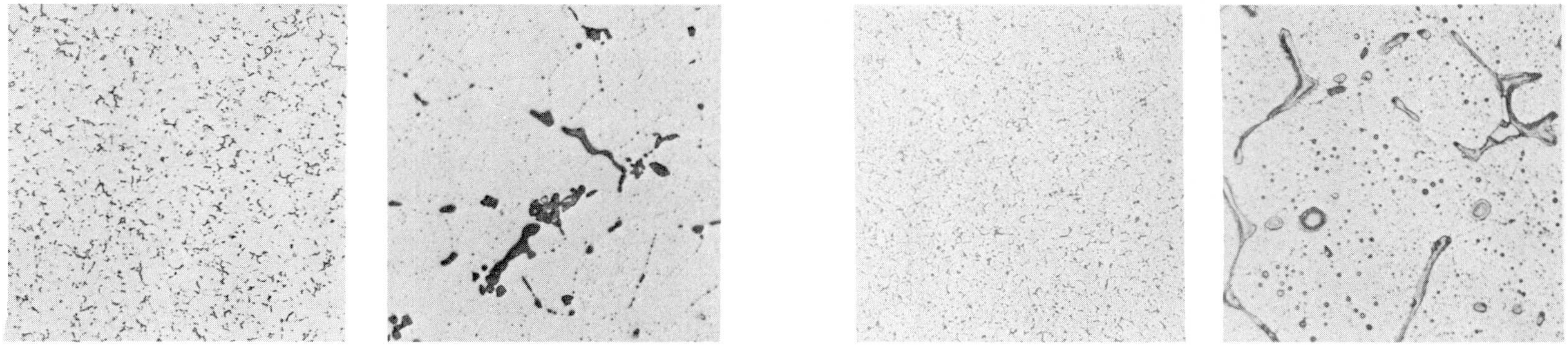
The microstructures of induction-melted as-cast Th, and the 1, 5, and 13 w/o U alloys are presented in Figure 9. Uranium not retained in solid solution was found to be precipitated at the grain boundaries or finely dispersed throughout the grains. The total amount of precipitate is shown to be a direct function of the w/o U in the Th. The structure of Th-13 w/o U exhibits significantly more grain boundary and intragranular precipitation over the lower uranium alloys. There is also evidence of grain refinement with increasing uranium content. The tendency appears to be for insoluble uranium to precipitate initially at the grain boundaries and then, with increasing percent uranium, within the grain. The large grey-black particles randomly distributed are inclusions.

The difference in grain size observed at the top and bottom on the cast ingots was a result of the mold and crucible arrangement. The top of the mold was in closer proximity to the molten charge, and was therefore at a higher temperature prior to pouring. Also, the initial poured metal had to traverse a greater distance before contacting the mold, thus losing some of its superheat. As a result, the metal at the base of the ingot had somewhat smaller grains, having had less opportunity for grain growth than its counterpart at the top of the ingot. Average grain size varied from ASTM-4.5 (0.085 mm diameter) at the top to ASTM-6.0 (0.050 mm diameter) at the bottom.



a. 100% Th

b. Th-1 wt % U



c. Th-5 wt% U

d. Th-13 wt% U

Figure 9. Microstructures of Induction Melted As-Cast Th and Th-U Alloys

IV. CONCLUSIONS

For a given melting cycle, the Y_2O_3 wash coating appears to be much more effective in preventing carbon contamination than ThO_2 or BeO. ZrO_2 stabilized with 15 w/o Y_2O_3 was approximately 90% as effective as Y_2O_3, whereas flame-sprayed ZrO_2 stabilized with CaO resulted in a slight advantage over wash-coated pure Y_2O_3. However, flame-sprayed coatings had the disadvantage of costing considerably more to apply than did wash coatings.

Minimizing both the molten time and pouring temperature results in a significant decrease in carbon contamination. At a pouring temperature of 1800°C, a decrease in molten time from 7 to 4 minutes reduced carbon pickup in a Th-13 w/o U alloy by a factor of 2.5. At a pouring temperature of 1830°C, a decrease in molten time from 7 to 4 minutes reduced carbon pickup by a factor of 3.6.

Flame-sprayed coatings were found to be more adherent, more thermal shock resistant, and somewhat more porous than wash coatings. Material for flame spraying includes relatively few fines, the converse being true for wash materials. Both techniques require close process control to achieve a continuous coating of uniform thickness. Additional development effort is needed to evaluate Y_2O_3 as a flame-sprayed coating on graphite.

As a matter of interest, a further reduction in contamination by carbon and other interstitial impurities may be achieved by melting larger quantities of alloy per given heat. The average charge of 5 kgs used in this investigation represented a surface/volume ratio of 0.595 cm^{-1}. If the charge were increased to 25 kgs in the same size and shape of crucible, the surface/volume ratio would decrease to 0.389 cm^{-1} and a corresponding 35% decrease in the carbon pickup could be realized.

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