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THORIUM ALLOYS; THE THORIUM-BISMUTH SYSTEM*

By Harlan B. Johnson

INTRODUCTION

This investigation of the thorium-bismuth system has been an outgrowth of work in the reduction of thorium fluoride to thorium metal. It had been suggested earlier that thorium containing a trace of bismuth might possess superior mechanical properties. Also, it was suggested that bismuth fluoride might be a more satisfactory booster for the reaction than the zinc chloride now used in the large scale production. Although it was found early in the work that a low melting, compact alloy could not be produced in good yield, the investigation was continued to the extent of making the following preliminary survey of the system. The only other mention of this system in the literature is the study by Russell, Nelson, and Grenell¹ on the erosion of thorium by a lead-bismuth eutectic. They observed the formation of a black compound between thorium and bismuth and noted considerable erosion of the thorium by bismuth at 900 to 1000°C.

SURVEY OF METHODS FOR ALLOYING THORIUM

Up until 1942 the only thorium binary system which had received any thorough study was the thorium-aluminum system. Leber,² by whom the thorium-aluminum system was investigated, prepared alloys up to 25 per cent thorium by weight through the reduction of $KThF_5$ with molten aluminum. Alloys higher in thorium were prepared by treating the low thorium alloys with more thorium metal. In order to inhibit oxidation it was necessary to work in an atmosphere of argon. This system was investigated only up to 56 per cent aluminum.

Grube and Botzenhardt³ investigated the binary systems of thorium with copper, aluminum, and sodium. The thorium-copper alloys were prepared by pressing mixtures of the powders into rods. These were sintered below the melting point. This was carried out in argon. Some difficulty was encountered in melting the metals together because of the oxide skin on the thorium.

These investigators repeated Leber's work on the thorium-aluminum system. Their attempts to prepare alloys by melting the metals together

*Work performed under Contract No. W-7405-Eng-82.

proved impractical since the reaction was extremely slow. It was possible to prepare the sodium-thorium alloys by simply heating the metals together. In none of these cases was the diagram completed over to 100 per cent thorium because of the difficulty of handling the highly reactive thorium-rich alloys.

Following a suggestion of Guertler⁴ that thorium might have certain uses as an alloying element for the heavy metals, Raub and Engel⁵ studied the binary systems of thorium with copper, gold, and silver. It was possible to prepare the low thorium alloys by sintering pressed powder rods. These investigators mention that difficulty was encountered in preparing thorium-rich alloys free from oxide because of the extreme reactivity. They described these alloys as "extraordinarily pyrophoric."

The report of a patent⁶ of the firm Siemens and Halske claims that low melting alloys of thorium can be prepared by treating thorium with lead, tin, zinc, cadmium, aluminum, and copper. The purpose of this was to allow nonmetallic impurities to separate at a temperature lower than the melting point of thorium. The statement that thorium exists in these alloys in the elementary state appears to be open to question since it is now known that compounds are formed in the case of lead, zinc, aluminum, and copper. However, the fact that bismuth was omitted from this list might possibly be taken to indicate that either no low melting alloy was produced or some difficulty was encountered in the preparation of the alloy.

Bernstorff and Allendorfer⁷ have devised a method for preparing alloys of reactive metals (Be, Ti, Zr, Th, or W) with less reactive metals (Cu, Fe, Mo, and Ni). The powders of the two metals were mixed together and pressed. This mixture was then surrounded by a casing of the less reactive metal and sintered below the melting point. This preliminary alloy was then used to introduce quantities of the reactive metal into more of the unreactive metal.

It is evident from these discussions that most thorium alloys, especially the thorium-rich alloys, are characterized by extreme reactivity. For this reason, and in some cases because of the high melting nature of thorium, it has been necessary to devise special methods for the preparation and handling of these alloys.

PREPARATION OF THORIUM-BISMUTH ALLOYS

Treatment of Thorium with Molten Bismuth

Early attempts to prepare alloys by melting the metals together were unsuccessful. Small blocks of thorium were treated with molten bismuth at 1300°C for periods up to 1 hr. This was carried out under an atmosphere of argon to prevent oxidation. Some reaction was observed but too little to be of use in preparing a massive alloy. Also the vaporization of bismuth begins to be troublesome at about 1150°C. It was found subsequently that some high bismuth alloys could be prepared by treating thorium rolled to 0.002-in. thickness with bismuth under the conditions

just described. However, even in this range the bomb coreduction method discussed in the following section proved to be more convenient.

Coreduction of the Fluorides

1. Method for Thorium-rich* Alloys

a. Apparatus. The coreductions were carried out in an iron bomb made by welding a bottom plate in one end of a 12-in. section of $2\frac{1}{2}$ -in. pipe. The other end was threaded and provided with a pipe cap. A thermocouple well welded to the exterior of the bomb held the thermocouple junction at a position 4 in. above the bottom. The charges were fired in a gas furnace automatically controlled at 750°C .

b. Materials. The calcium used as reductant was obtained from the Electrometallurgical Company. A technical grade of bismuth fluoride supplied by the Harshaw Chemical Company was used as a source of bismuth and also as a booster for the reduction of the thorium fluoride. This bismuth fluoride analyzed at 15.9 per cent fluoride as compared to the calculated value of 21.4 per cent. One batch of bismuth fluoride prepared in this laboratory analyzed at 21.4 per cent fluoride. This was used in several reductions, but no significant difference in the product was noted. The thorium fluoride was prepared in this laboratory by hydrofluorination of the oxide and analyzed 99.5 per cent ThF_4 . The bomb liner was a sintered dolomitic oxide crucible which held the charge. This crucible was packed into the bomb using electrolytically fused dolomitic oxide as an outside filler.

c. Procedure. The charge was prepared by mixing thoroughly the appropriate proportions of thorium fluoride, bismuth fluoride, and calcium. This mixture was then tamped firmly into the liner, and the remaining space packed with electrolytically fused dolomitic oxide. After tightening the cap securely, the thermocouple was placed in the well and the assembly suspended in the furnace. The heating and firing temperatures were followed on a potentiometer located at a remote station. The charges fired at about 500°C after a heating period of 10 min. At this point a significant increase in the rate of heating indicated that the reaction had taken place. When the rapid increase in heating had subsided (after about 2 min), the bomb was removed from the furnace and allowed to cool at room temperature overnight.

The bomb was opened the following day and the fused slag and liner were chipped away from the metallic biscuit. The thorium-bismuth intermetallic compounds are pyrophoric and oxidize rapidly in the air, especially in moist air. The samples were stored most satisfactorily over Drierite in an atmosphere of argon. Even under these conditions, however, occasional exposure to the air caused rapid oxidation and disintegration of the biscuits.

*The term, "thorium-rich," as used in this report, indicates those alloys containing at least 66.7 mole per cent thorium.

2. Method for Bismuth-rich* Alloys

These runs were very similar to those described for thorium-rich alloys, the main difference being that granulated bismuth was added to the charges in appropriate amounts. It was found that direct reduction of the fluorides in the proportions calculated to produce bismuth-rich alloys apparently yielded bismuth-calcium alloys since thorium could not be detected in the analysis. Bismuth was present to the extent of approximately 85 per cent in the latter alloys.

3. Method for Intermediate Alloys

When powdered thorium became available, an attempt was made to prepare alloys ranging in composition from 66.6 to 25 per cent Th. The thorium powder had been produced by decomposition of the hydride. Powdered bismuth was produced simply by grinding the metal in a mortar. Both powders passed a 30-mesh screen.

Suitable mixtures of the metal powders were pressed into compact rods and heated at 1000°C for 1 hr in close fitting crucibles. The heating was carried out, and the alloys were allowed to cool overnight under vacuum. When the products were removed, they burst into flame with almost explosive violence on contact with the air. No satisfactory method was worked out for handling these alloys.

STUDIES ON THORIUM-RICH ALLOYS

Microscopic Examination

1. Polishing Methods and Materials

Since the compound phase oxidized very rapidly, it was necessary to carry through the polishing on the wheels and papers without delay. It was frequently found necessary to sacrifice something in the refinement of the operation in order to retain some of the structure of the compound. Two methods were used for the final polishing on the wet wheel. Neither method yielded entirely satisfactory results. The structures shown in Figs. 1, 2, 3, and 6 were polished on the wet wheel using a suspension of levigated alumina powder in mineral oil. The structures shown in Figs. 4 and 5 were polished quite briefly on the wet wheel with a suspension of alumina in aqueous soap solution. These were washed immediately with acetone and dried in a stream of warm air.

2. Photomicrographs

Since no method for preserving the polished surfaces was found, the photomicrographs were made within a few seconds after the sample had

*The term, "bismuth-rich," as used in this report, indicates those alloys containing at least 75 mole per cent bismuth.

been polished. These pictures were taken with the aid of a Bausch and Lomb metallograph. All magnifications are at 50X.

3. Discussion of Microstructures

In Fig. 1 the gray, dendritic thorium phase is seen together with a eutectic structure. As the percentage of thorium decreases in the following figures, the thorium phase decreases and the compound phase increases until a structure consisting almost entirely of compound is noted in Fig. 6. The analysis of this sample suggested a compound having the approximate formula, Th_2Bi . Solely on the basis of these photomicrographs, it is suggested tentatively that the eutectic in this region lies at about 20 per cent bismuth. No method was readily available by which this could be positively established.

Thermal Studies

1. Cooling Curves

No thermal arrests were observed in the range of the chromel-alumel thermocouple (below 1325°C). Several attempts were made to investigate the higher temperature ranges using a tungsten-columbium thermocouple. In each case the thermocouple failed, however, and this method of study was abandoned. In any case, study of the molten alloys would almost certainly be complicated by considerable contamination from the oxides of thorium and bismuth. Also the low heat of fusion of thorium would make the detection of a liquidus extremely difficult in this region.

2. Melting Points

a. Equipment. A beryllia crucible 4 in. in depth and having an inside diameter of $1\frac{5}{8}$ in. was fitted internally with a beryllia cylinder 1 in. in length which rested on the bottom of the crucible. The crucible was provided with a beryllia cover with a $\frac{1}{2}$ -in. hole in the center. This assembly was enclosed in a graphite heater and arranged for heating under vacuum in the induction furnace. A $1\frac{1}{4}$ -in. thorium rod $1\frac{1}{2}$ ft in length was capped with beryllia at one end. The vacuum head was fitted with an observation tube up into which the other end of the thorium rod could extend. The observation tube contained a plane glass window to facilitate readings by optical pyrometer.

b. Procedure. A strip of an alloy was obtained which measured $1\frac{1}{2}$ in. by $\frac{1}{2}$ in. by $1/8$ in. A v-notch $1/16$ in. deep was ground transversely across the center of the strip. The strip was then supported diametrically on the beryllia ring with the notch on the under side. The capped end of the thorium rod was allowed to rest on the center of the strip with the other end extended up into the observation tube.

The temperature was raised to the melting point during the course of 40 to 50 minutes. As the region of the melting point was approached, the temperature of the strip was followed closely by means of an optical

pyrometer. When the melting point has been reached, the rod could be seen to drop. This temperature was noted and taken as the melting point.

c. Discussion of Melting Points. In Table 1 are listed several melting points obtained by the procedure just described. An average value of these results was found to be 1350°C . The variations are perhaps due to varying stages of oxidation of the surface of the sample. It is known in other cases that thorium tends to form a tough skin of oxide which resists deformation to a surprising degree.

Table 1--Melting Points of Thorium Rich Alloys

Bi, %	mp
9.2	1365°C
18.5	1335°C
18.9	1375°C
23.0	1340°C

Difficulty in obtaining homogeneous alloy strips free from slag made it impossible to get melting points on samples of higher bismuth content.

STUDIES ON BISMUTH-RICH ALLOYS

Thermal Analysis

The bismuth-rich alloys prepared by the method of coreduction presented a highly crystalline cellular structure. This is shown in the actual size in Figure 7. When these alloys were heated to 1200°C and allowed to cool, the only thermal arrest evident was at 271°C , the melting point of bismuth. This indicated the absence of any detectable eutectic. The crystalline structure refused to melt under these conditions. These structures appeared to consist of a framework of compound platelets coated with free bismuth.

Solubility of Thorium in Molten Bismuth

During the course of the work of attempting to prepare alloys by treating small blocks of thorium with molten bismuth, it was observed that platelets of compound precipitated out of the bismuth in such a manner as to indicate that equilibrium had been reached. Analysis of this equilibrium mixture, then, should give the solubility of thorium, as compound, in bismuth at the temperature at which the treatment was carried out. At 700°C a mixture obtained after heating 3 hr analyzed 1.5 per cent thorium. At 1100°C a mixture obtained by heating an excess of thorium foil with bismuth for 30 min analyzed 2.2 per cent thorium.

One of the crystalline samples obtained by coreduction was heated on a sintered glass filter to 290°C and held at this temperature for 15 min.

The molten metal was then centrifuged through the filter at 15,000 rpm. No thorium was detected in the analysis of this sample. However, a slight impurity was evident in the microstructure. This was apparently a trace of compound. This method could be applied more extensively in the uranium-bismuth system.⁸

Discussion of Bismuth-Rich Alloys

Thorium is evidently only very slightly soluble in bismuth in the range of temperatures that could be investigated. The thermal data and microscopic study indicate the absence of a eutectic in this region. Here again, the vaporization of bismuth precluded any attempt to investigate the higher temperature regions.

THORIUM-BISMUTH COMPOUNDS

The Thorium-Rich Compound

1. The Flotation Separation

Three of the thorium-rich samples of different compositions were covered with water and allowed to stand for two to four weeks until the biscuits had completely decomposed, and the compounds had been converted to the oxides. A steady evolution of hydrogen was observed during this time. When the decomposition was complete, the black powder mixture obtained was transferred to a large beaker, and water was added to 1 1/2 liters. The mixture was stirred mechanically for 2 hr and then allowed to stand for 1 min. At the end of this time the top one liter of suspension was removed through a tube connected to a suction flask.

It was expected that this procedure should effect a separation of the thorium and bismuth oxides from the more dense particles of free thorium. The aqueous suspension was evaporated to dryness, and the mixture of oxides was submitted for analysis. Table 2 lists the results obtained by this method. These values were helpful in confirming the formula suggested in connection with the study of the microstructures as approximately Th_2Bi .

Table 2--Thorium-Rich Compound

Th in sample, %	Ratio, Th/Bi
90	2.17
85	2.23
80	2.18

2. The Acid Separation

A biscuit containing 18.9 per cent Bi was allowed to oxidize and disintegrate under water. The mixture was evaporated to dryness and then treated with concentrated nitric acid. The mixture was heated at boiling for 1 hr and filtered through a sintered glass filter. The filtrate was analyzed for the ratio of thorium to bismuth. Two runs yielded ratios of 2.05 and 2.02.

3. Discussion of Yields

Since the success of the bomb reduction method depends on the production of a relatively low melting metal, it was to be expected that as the composition of the compound was approached, the yield should decrease. This was found to be the case. In fact, a biscuit of the exact composition, Th_2Bi , was never produced despite repeated attempts. The structure shown in Fig. 6 was the closest approach. Even in this case the metal did not form a well shaped biscuit and it was impossible to separate from the slag. This decrease in yield is shown in Table 3 where the mole ratio of thorium to bismuth in the original charge is listed together with the per cent yields. The mole ratio of Th/Bi in the product is given also.

Table 3--Coreduction Data

Charge Ratio, Th/Bi	Yield, %	Product Ratio, Th/Bi
5.0	87	8.8
3.6	78	5.3
2.4	66	3.9
2.0	49	3.9
1.7	51	2.60
1.5	42	2.56
1.35	47	3.7
1.25	small	2.34
1.00	small	--
0.90	small	--
0.67	small	--
0.47	small	--
0.34	small	--
0.23	small	--

It can be seen from Table 3 that as the charge ratio, Th/Bi, decreases, the yield also decreases. Although a smooth curve could not be plotted from these values, the general trend seems definite. The products obtained from charge ratios of 1.25 or less yielded only a trace of metal or no metal at all in the bottom of the liner. It is to be noted that even in those cases where the charge ratio was less than 2.00, no biscuit was obtained having a ratio, Th/Bi, smaller than

2.00. It appears likely that the product ratio approaches 2.00 as a limiting value. This then may serve as additional evidence of a compound having a formula which approximates Th_2Bi very closely.

4. Melting Point of the Thorium-rich Compound

Since an alloy of the composition Th_2Bi could not be prepared readily, it was not possible to obtain the melting point of this compound. In view of the diminishing yields, however, it is probable that this melting point is considerably higher than 1350°C . Also, this melting point is evidently below 1900°C . Three thorium biscuits containing 1 per cent bismuth were cast into small billets at 1900°C . During this operation the bismuth content was reduced to 0.1 per cent. This may indicate that no compound in the system is stable at this temperature. Figure 8 shows the microstructure at 250X of a billet containing 0.1 per cent bismuth. The white phase at the crystal boundaries appears frequently in thorium cast in BeO crucibles. The dark phase is the Th- Th_2Bi eutectic.

The Bismuth-rich Compound

1. The Flotation Separation

The procedure described in the previous section was repeated using bismuth-rich biscuits. The bismuth-rich compound seemed to be slightly less reactive than the thorium-rich compound but reacted with water readily. Table 4 gives the results obtained. The average of these ratios suggests a compound of the approximate formula, ThBi_3 .

Table 4--Bismuth-rich Compound

Bi in Sample, %	Ratio, Bi/Th
89	2.78
80	3.40
90	2.97

2. The Acid-amalgam Separation

A biscuit containing 89 per cent bismuth was treated with mercury and concentrated HCl. The mixture was stirred until the amalgamation of the bismuth and the solution of the compound were complete. The acid solution was decanted and analyzed. This method gave Bi/Th ratios of 3.29 and 3.17 on two runs. These values check well with those given in Table 4.

X-ray Investigation

Several attempts were made by the X-ray group to obtain powder diagrams of both the thorium-rich alloys and the bismuth-rich alloys.

These attempts in each case met with failure apparently due to the rapid oxidation of the compounds in the finely divided form. This was unfortunate since this method might have yielded a positive identification of the compounds.⁹

Diffusion Studies

Diffusion studies were carried out by treating small blocks of thorium with molten bismuth at various temperatures and for varying lengths of time. The reaction at the interface was then noted. During 16-hr heating periods only a very slight reaction was observed below 500°C. At 560°C the reaction shown in Fig. 9 was obtained. The magnification is 150X. The thorium-rich compound is seen as a narrow band against the thorium, while the bismuth-rich compound is a broader lighter colored region.

The reaction shown in Fig. 10 was obtained by heating 2 hr at 700°C. The thorium-rich compound has been washed out considerably in polishing. There was no indication of a third compound in these studies.

CHEMICAL ANALYSIS FOR THORIUM AND BISMUTH

Determination of Bismuth

A dilute nitric acid solution of thorium and bismuth with traces of calcium was treated with H_2S to precipitate bismuth sulfide. This precipitate was washed thoroughly with water treated with more H_2S . The bismuth sulfide was then dissolved in 1:1 nitric acid. This solution was carefully neutralized with ammonium hydroxide and treated with secondary ammonium phosphate. The filtered and dried precipitate was weighed as bismuth phosphate.

Determination of Thorium

The dilute acid solution of thorium sulfide was boiled to remove the H_2S . Ammonium hydroxide was added to the end point as indicated by phenolphthalein. The precipitate of thorium hydroxide was filtered effecting a separation from calcium. The hydroxide was dissolved in nitric acid and precipitated with oxalic acid. This filtered and dried precipitate was weighed as thorium oxide.

Discussion of Chemical Analysis

Three samples were run on each sample submitted. In general, more satisfactory checks were obtained from the thorium-rich samples than from those rich in bismuth. Some difficulty was encountered in washing the bismuth sulfide precipitate free from thorium.

EQUILIBRIUM DIAGRAM AND DISCUSSION

Portions of the equilibrium diagram of thorium and bismuth are shown in Fig. 11. As indicated in earlier discussions, little is known of the composition range from 33.3 to 75.0 per cent Bi. However, the fact that no yield was obtained by the coreductions in this range indicates that melting occurs substantially above 1350°. The ready formation of oxides in this region might also be a complicating factor. Also, no third compound was observed by means of the diffusion studies.

Two biscuits containing more than 75 per cent bismuth were heated to 1500 to 1600°C under vacuum in order to distill off the free bismuth. The residues were in the intermediate range of composition. Apparently the decomposition point of ThBi_3 had been exceeded. The difficulty in obtaining satisfactory analyses and the inability to study microstructures made work in this region somewhat more uncertain than at the thorium-rich end of the system.

During the early work with the flotation method, it was hoped that a general method might be developed for the identification of extraordinarily reactive intermetallic compounds. Since only approximate results were obtained, however, the usefulness of this method is apparently limited to cases in which the composition of the compound is not readily identified by other means.

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Fig. 1--Bi 9.2 per cent.

Fig. 2--Bi 14.5 per cent.

Fig. 3--Bi 18.8 per cent.

Fig. 4--Bi 23.0 per cent.

Fig. 5--Bi 25.7 per cent.

Fig. 6--Bi 32.6 per cent.

Fig. 7--Bi 83.5 per cent.
(actual size).

Fig. 8--Bi 0.1 per cent (250X).

079

013

Fig. 9--Th-Bi reaction
at 560°C (150X).

Fig. 10--Th-Bi reaction
at 700°C (250X).

Fig. 11--The thorium-bismuth capture.