April 21, 1964 R. J. TEITEL 3,130,042

PROCESSING THORIUM-BISMUTH AND THORIUM-LEAD COMPOUNDS

Filed Aug. 2, 1961 2 Sheets-Sheet 1

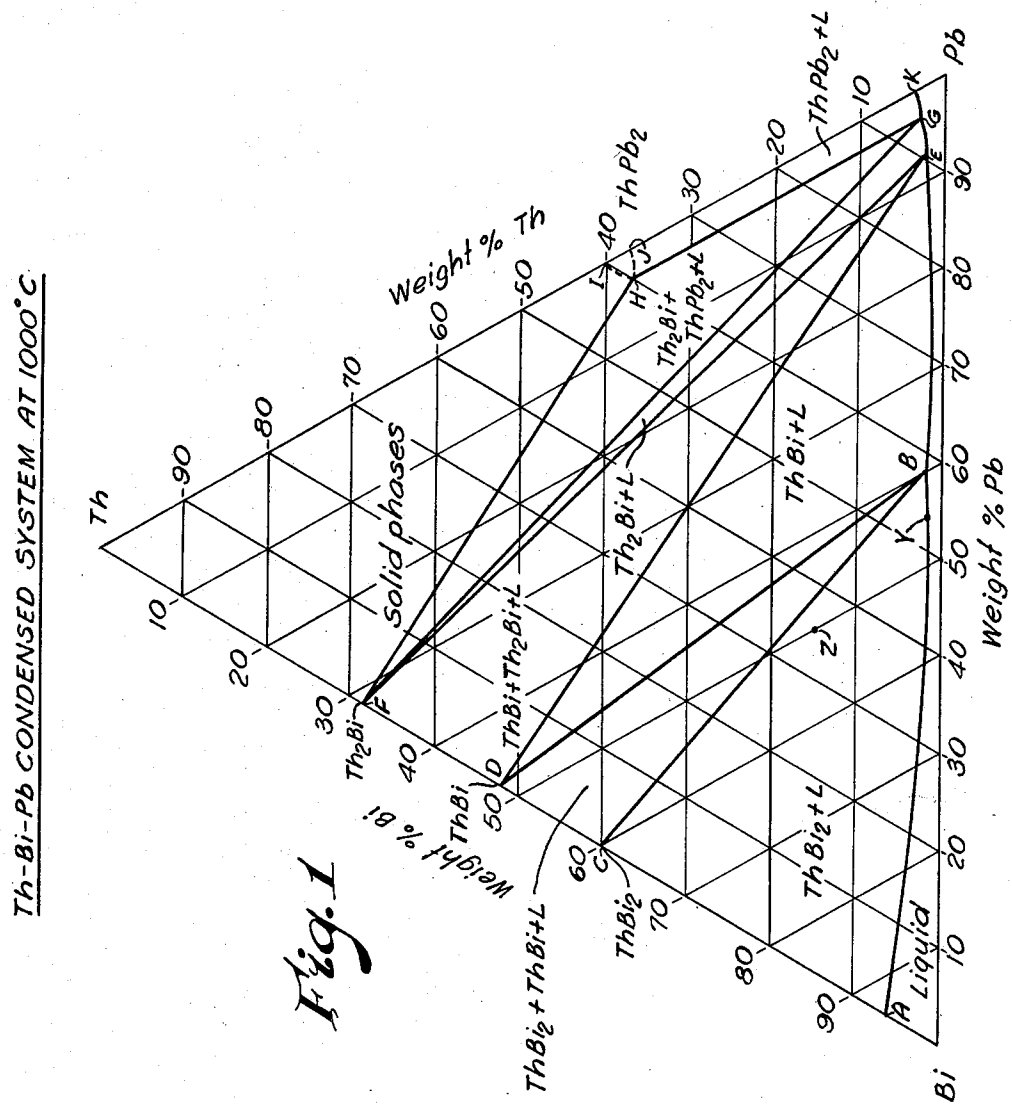


Fig. 1

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Th-Bi-Pb CONDENSED SYSTEM AT 1000°C WITH SUPERIMPOSED AREAS FOR OTHER TEMPERATURES

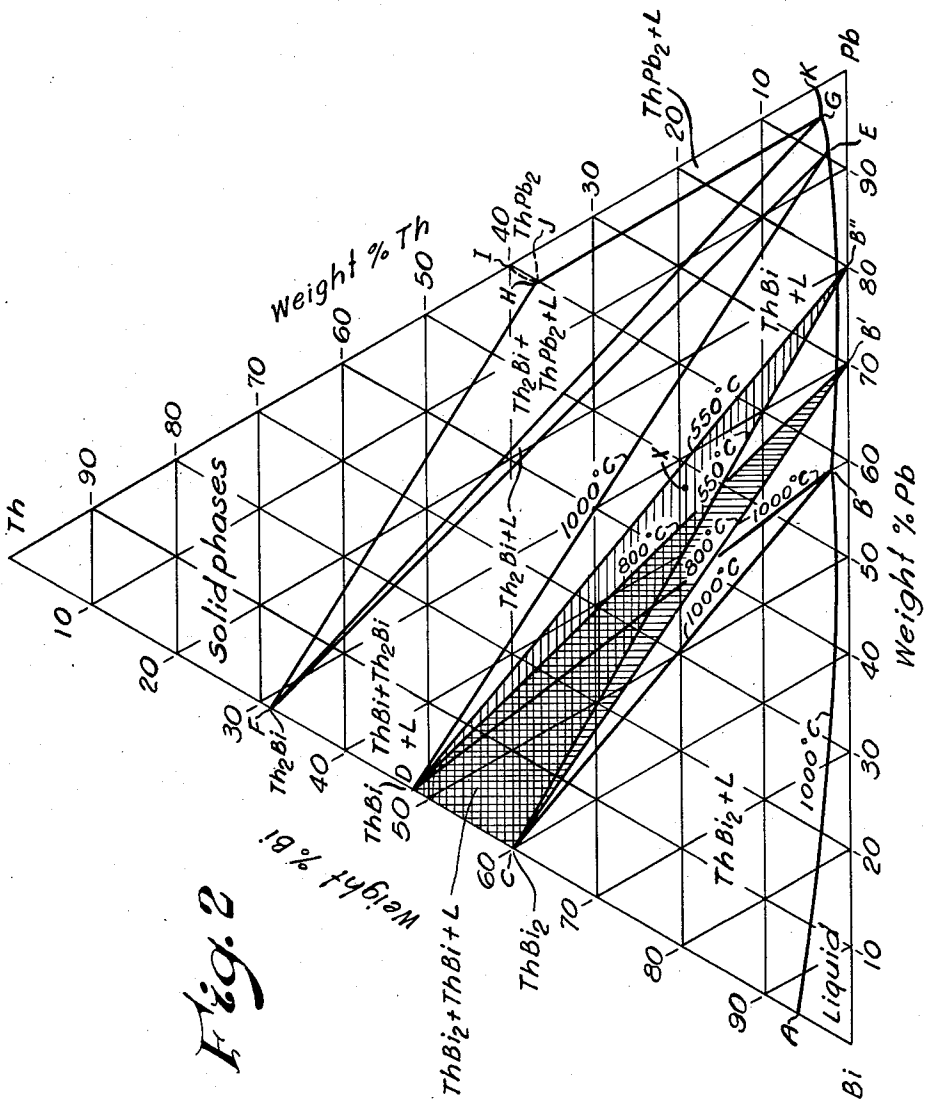


Fig. 2

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United States Patent Office 3,130,042 Patented Apr. 21, 1964

3,130,042
PROCESSING THORIUM-BISMUTH AND THORIUM-LEAD COMPOUNDS

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Filed Aug. 2, 1961, Ser. No. 128,827
9 Claims. (Cl. 75—84.1)

The invention relates to an improved method of recovering uranium entrapped or occluded within solid particulate thorium-bismuth or thorium-lead intermetallic compound.

Heretofore attempts have been made to recover the uranium isotope having an atomic number of 233, hereinafter referred to as U^{233}, from neutron irradiated thorium-bismuth compound by completely dissolving the thorium in bismuth or bismuth-lead alloy. But this has required the use of processing temperatures above 1000° C., and, in addition, subsequent cooling must be carefully controlled in order to arrive again at a thorium compound dispersion having particulate compound of suitable particle size and shape. In other attempts to free uranium from thorium intermetallic compound dispersion the compound has been broken up mechanically by grinding or by sonics, but mechanical treatments require the use of additional apparatus and are not well adapted to be carried out by remote control.

It is therefore a principal object of the invention to provide a method of recovering uranium, from a thorium intermetallic compound with bismuth or lead having uranium occluded therein, by a process which does not require the use of temperatures as high as 1000° C. and which is adapted to be carried out remotely with relative simplicity.

For the purpose of the specification and claims: (1) bismuth and any of the bismuth-lead binary alloys are referred to as a bismuth metal, (2) molten lead or a molten bismuth metal is referred to as a liquid metal, (3) thorium intermetallic compound refers to thorium-bismuth or thorium-lead intermetallic compound, and (4) occluded uranium includes coprecipitated uranium as well as uranium generated by neutronic irradiation of thorium.

FIG. 1 is a trilateral graph on which there is indicated the phases present in delineated composition ranges for the condensed system Th—Bi—Pb at 1000° C.; and

FIG. 2 is a similar trilateral graph on which there is indicated the changes, with temperature, in boundary limits for some of the composition ranges delineated in FIG. 1.

The improved process of the invention is based on the discovery that upon subjecting a solid particulate thorium intermetallic compound to at least one of temperature and liquid metal composition changes to cause the intermetallic compound to convert to another solid particulate intermetallic compound while at all times retaining both a solid and a liquid phase, as hereinafter more fully explained, uranium is effectively exposed to the liquid phase and dissolved therein, and upon separating the liquid phase from the dispersion, uranium is recovered as an alloy of the liquid metal.

Thorium intermetallic compounds which may be processed according to the invention include $ThBi_2$, ThBi, Th_2Bi, $ThPb_2$ and $ThPb_3$. The compounds usually involved in liquid metal fuel are $ThBi_2$ and ThBi.

The liquid metal used in desirably a bismuth metal containing from about 30 to 80 percent of lead, the balance bismuth.

In FIG. 1 is shown a conventional phase diagram, as understood in the fields of physical chemistry and metallurgy, for the condensed ternary system Th—Bi—Pb at 1000° C. The three corners of the diagram each represent 100 percent of the element denoted by adjacent symbol. The solid lines superimposed on the grid delineate ranges of composition in which a specified number of phases co-exist in equilibrium. For example, the area bounded by the lines connecting points A, B, and C represents a range of total compositions which if brought to and maintained at 1000° C. under equilibrium conditions will contain one solid phase, $ThBi_2$, and one liquid phase. The area bounded by the lines connecting points B, C and D similarly represents a range of compositions which under equilibrium conditions at 1000° C. will contain two solid phases, $ThBi_2$ and ThBi, and one liquid phase, the liquid phase having the composition represented by point B. The area bounded by the lines connecting points B, D and E represents a range of compositions which under equilibrium conditions at 1000° C. will contain one solid phase, ThBi, and one liquid phase. The area bounded by the lines connecting points D, E and F represents a range of compositions which under equilibrium conditions at 1000° C. will contain two solid phases, ThBi and Th_2Bi, and one liquid phase having a composition represented by the point E. Compositions represented by the area below the lines connecting points A, B, E, G and K are entirely liquid at 1000° C. The character of the other areas is apparent from the legends employed in the drawings.

In carrying out the process of the invention, as indicated hereinabove, a solid particulate thorium intermetallic compound dispersed in a liquid metal is caused to convert to a different solid particulate thorium intermetallic compound by composition or temperature change or both.

Referring to FIG. 1, it may be seen that a total composition represented on the diagram by the point at Z, and containing, by weight, 15 percent of thorium, 50 percent of bismuth, and 35 percent of lead, will, at 1000° C., consist of $ThBi_2$ in equilibrium with liquid of the composition represented by the point Y. Upon increasing the concentration of lead in the composition to at least 54 percent, while maintaining a temperature of about 1000° C., the $ThBi_2$ will gradually convert entirely to ThBi plus liquid metal. Then upon bringing the bismuth concentration of that same composition to at least 46 percent the ThBi plus liquid metal will gradually convert entirely to $ThBi_2$ plus liquid metal. At all times during these transitions there will be present both a solid and a liquid phase since the composition is not entirely liquid except at temperatures well above 1000° C., or unless the thorium concentration falls in the area of the graph below line ABEGK.

The foregoing composition changes or cycles may be employed one or more times where the metal composition is receiving a terminal treatment, as before disposal. However, in systems such as circulated or reused reactor blanket streams it is essential to maintain the concentration of thorium at reasonable concentrations to effect efficient neutron capture. Under those circumstances, dilution of the composition with the requisite amounts of lead and bismuth to create conditions favoring, alternately, different solid phases, leads to great increases in the volume of the composition. It is thus generally more convenient and practical to carry out temperature changes, or cycling, with no change or with only small changes in composition.

The use of temperature changes will be more clearly understood with reference to FIG. 2. In FIG. 2 there is shown the effect of temperature on the range of compositions in which $ThBi_2$ and ThBi both exist in equilibrium with liquid metal. The three lines connecting points B, C and D define the area for 1000° C., while the lines connecting points B', C and D define the area at 800°

C., and the lines connecting points B'', C and D define the area at 550° C., equilibrium conditions prevailing at each temperature. The remainder of the diagram is the same as that shown in FIG. 1.

A total composition represented by point X, on the diagram of FIG. 2, contains $ThBi_2$ plus liquid under equilibrium conditions at 550° C. It may be seen from FIG. 2 that upon bringing the composition represented by point X to 800° C., the composition contains $ThBi_2$ and ThBi in equilibrium with liquid metal of composition B'. And upon bringing the same composition to 1000° C. for a period of time to establish equilibrium conditions, the composition consists of $ThBi_2$ plus liquid metal.

As an illustration of another manner of carrying out the present method, a composition represented by the point X in FIG. 2 consists of $ThBi_2$+liquid metal at 550° C. under conditions of stable equilibrium. Upon heating the composition to 800° C. and bringing the lead content of the composition to at least 53 percent the composition will consist of ThBi+liquid metal, once equilibrium is re-established. And on cooling the so-modified composition to 550° C., the phases present will again consist of $ThBi_2$+liquid metal under equilibrium conditions. The complete conversion of $ThBi_2$ to ThBi and the converse is thus completed with a modicum of composition alteration and under a less severe temperature environment.

The method is not limited to changes involving $ThBi_2$ and ThBi only, but, if desired, may be carried out in a similar manner to any of the methods illustrated above under composition and temperature conditions whereby Th_2Bi or $ThPb_2$ are involved, as may be understood from FIGS. 1 and 2, or at lower temperature $ThPb_3$ may be involved at low bismuth concentrations, e.g., below about 4 percent of bismuth.

To illustrate the behavior of uranium metal taken up and precipitated in a thorium intermetallic compound dispersion whereby the uranium is occluded within the intermetallic compound, 650 grams of lead and 300 grams of bismuth were melted together in an outgassed graphite crucible within an electric furnace under a helium atmosphere, and heated to 650° C. Then 50 grams of thorium was added to the melt which was agitated about every ½ hour for 5 hours whereby a dispersion of $ThBi_2$ was formed. The temperature of the furnace and contents was reduced to 500° C. and 150 milligrams of uranium chips in a perforated graphite cup were lowered through a gas lock located on top of the furnace and inserted into the melt. The uranium was allowed to dissolved during a 17 hour period while the temperature was maintained at 500° C. Two samples of the liquid phase, of about 8 grams each, were withdrawn through a graphite frit enclosed tube. Then the composition was heated to and maintained at 800° C. for 30 minutes during which time the transformation of $ThBi_2$ to ThBi was complete. The liquid phase was sampled in the same manner as before. The composition was then allowed to cool to 650° C. and maintained at that temperature for 30 minutes. During this time the ThBi reverted to $ThBi_2$. The liquid phase was again sampled. The composition was held at 400° C. for about 17 hours and the liquid phase was sampled. The composition was then taken through the heating and holding cycle two more times, samples being withdrawn each time after a period for equilibrium at 800° C., 650° C., and at 400° C. Then the composition was allowed to solidify as a casting and examined.

Chemical analyses of the liquid phase samples showed that the concentration of uranium in the liquid phase was duplicated through each cycle and that about 33 percent, 10 percent and 2.5 percent of the total uranium was present in the liquid phase at 800° C., 650° C. and 400° C., respectively.

Metallographic examination of the lower part of the casting containing settled $ThBi_2$ showed that the particles of $ThBi_2$ were finely divided and uniformly dispersed, the particle sizes ranging from about 5 to 40 microns diameter and most of the particles having a diameter in the range of 10 to 15 microns. Chemical analysis showed that the settled layer contained 11.6 percent by weight of thorium.

Example

A 1200 gram charge of neutron-irradiated, settled dispersion of the thorium bismuthide, $ThBi_2$, consisting of 528 grams of lead, 168 grams of bismuth, 503 grams of $ThBi_2$, and 0.12 gram of U^{233}, is placed in a previously out-gassed graphite filter crucible in an electric furnace having means for providing a pressure differential across the porous graphite crucible. The furnace is purged of air and filled with helium. Then the charge is brought to and maintained at a temperature of 800° C. for 2 hours, after which the temperature is lowered to and maintained at 650° C. for 2 hours. The charge is then heated to and maintained at 800° C. for 2 hours and filtered into a collector consisting of a graphite crucible. The furnace is cooled to about 400° C. and then a charge consisting of 400 grams of a lead-bismuth alloy containing 80 percent of lead and 20 percent of bismuth is admitted to the filter crucible in the furnace via a gas lock. The filter crucible and contents is then heated to 800° C. and after about 30 minutes the contents of the filter crucible are again filtered, the filtrate being collected in the same collector crucible as before. The furnace is then allowed to cool and the contents of the collector crucible are sampled and analyzed radiochemically. The combined filtrates are found to contain significant quantities of U^{233}.

I claim:

1. The improved method of recovering uranium from a solid particulate thorium intermetallic compound selected from the group consisting of thorium-bismuth and thorium-lead compounds, said thorium intermetallic compound being dispersed in a liquid metal selected from the group consisting of bismuth, lead and bismuth-lead alloy, and having uranium occluded therein, which comprises: changing at least one of (1) the temperature of the said dispersion in liquid metal, and (2) the composition of the liquid metal, the change in said composition being brought about by the addition to the dispersion of a metal selected from the group consisting of lead, bismuth, thorium and mixtures thereof differing in composition from the dispersion, thereby to cause said solid particulate thorium intermetallic compound to convert to another solid particulate thorium intermetallic compound while at all times retaining both a solid and a liquid phase, and thereafter separating the liquid phase from the solid phase in the dispersion.

2. The improved method of recovering uranium from a solid particulate thorium intermetallic compound selected from the group consisting of thorium-bismuth and thorium-lead compounds, said thorium intermetallic compound being dispersed in a liquid metal selected from the group consisting of bismuth, lead and bismuth-lead alloy, and having uranium occluded therein, which comprises: changing (1) the temperature of the said dispersion in liquid metal, and (2) the composition of the liquid metal, the change in said composition being brought about by the addition to the dispersion of a metal selected from the group consisting of lead, bismuth, thorium and mixtures thereof differing in composition from the dispersion, thereby to cause said solid particulate thorium intermetallic compound to convert to another solid particulate thorium intermetallic compound while at all times retaining both a solid and a liquid phase, and thereafter separating the liquid phase from the solid phase in the dispersion.

3. The improved method of recovering uranium from a solid particulate thorium intermetallic compound selected from the group consisting of thorium-bismuth and

thorium-lead compounds, said thorium intermetallic compound being dispersed in a liquid metal selected from the group consisting of bismuth, lead and bismuth-lead alloy, and having uranium occluded therein, which comprises: changing the temperature of the said dispersion in liquid metal sufficiently to bring the dispersion into another equilibrium phase region, thereby to cause said solid particulate thorium intermetallic compound to convert to another solid particulate thorium intermetallic compound while at all times retaining both a solid and a liquid phase, and thereafter separating the liquid phase from the solid phase in the dispersion.

4. The improved method of recovering uranium from a solid particulate thorium intermetallic compound selected from the group consisting of thorium-bismuth and thorium-lead compounds, said thorium intermetallic compound being dispersed in a liquid metal selected from the group consisting of bismuth, lead and bismuth-lead alloy, and having uranium occluded therein, which comprises: changing the composition of the liquid metal by the addition thereto of a metal selected from the group consisting of lead, bismuth, thorium and mixtures thereof differing in composition from the dispersion, thereby to cause said solid particulate thorium intermetallic compound to convert to another solid particulate thorium intermetallic compound while at all times retaining both a solid and a liquid phase, and thereafter separating the liquid phase from the solid phase in the dispersion.

5. The improved method of recovering U^{233} as a bismuth metal alloy from a dispersion in a liquid bismuth metal of a neutron-irradiated, solid particulate thorium-bismuth intermetallic compound which comprises: changing at least one of (1) the temperature of the said dispersion and (2) the composition of the bismuth metal, the change in said composition being brought about by the addition to the dispersion of a metal selected from the group consisting of lead, bismuth, thorium and mixtures thereof differing in composition from the dispersion thereby to cause solid particulate thorium-bismuth intermetallic compound to convert to another solid particulate thorium-bismuth intermetallic compound, while at all times retaining both a solid and a liquid phase, and thereafter separating the liquid phase from the solid phase in the dispersion.

6. The improved method of recovering U^{233} as a bismuth metal alloy from a dispersion in a liquid bismuth metal of a neutron-irradiated solid particulate thorium-

bismuth intermetallic compound which comprises: changing at least one of (1) the temperature of the said dispersion and (2) the composition of the bismuth metal, the change in said composition being brought about by the addition to the dispersion of a metal selected from the group consisting of lead, bismuth, thorium and mixtures thereof differing in composition from the dispersion thereby to cause said solid particulate thorium-bismuth intermetallic compound to successively convert at least twice to successively different solid particulate thorium-bismuth intermetallic compounds while at all times retaining both a solid and a liquid phase, and thereafter separating the liquid phase from the solid phase in the dispersion.

7. The method as in claim 6 in which at least one of said temperature and bismuth metal composition changes is made cyclically.

8. The improved method of recovering U^{233} as a bismuth metal alloy from neutron-irradiated solid particulate $ThBi_2$ dispersed in a liquid bismuth metal which comprises: changing at least one of (1) the temperature of the said dispersion and (2) the composition of the bismuth metal, the change in said composition being brought about by the addition to the dispersion of a metal selected from the group consisting of lead, bismuth, thorium and mixtures thereof differing in composition from the dispersion, thereby to cause said $ThBi_2$ to convert to ThBi, while at all times retaining both a solid and a liquid phase, and thereafter separating the liquid phase from the solid phase in the dispersion.

9. The improved method of recovering U^{233} as a bismuth metal alloy from neutron-irradiated solid particulate $ThBi_2$ dispersed in a liquid bismuth metal which comprises: changing at least one of (1) the temperature of the said dispersion and (2) the composition of the bismuth metal, the change in said composition being brought about by the addition to the dispersion of a metal selected from the group consisting of lead, bismuth, thorium and mixtures thereof differing in composition from the dispersion, thereby to cause said $ThBi_2$ to convert to ThBi, and further to cause said ThBi to convert to the thorium-bismuth compound selected from the group consisting of $ThBi_2$ and Th_2Bi, while at all times retaining both a solid and a liquid phase throughout each of said changes, and thereafter separating the liquid phase from admixture with the solid phase.

No references cited.