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THORIUM ALLOY AND METHOD OF PREPARING THE SAME

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This invention relates to certain alloys of thorium with the refractory metals tungsten and molybdenum, and to methods of preparing such alloys in ductile form. The invention relates also to electron emitting devices embodying these alloys.

Efforts have been made in the past to alloy thorium in small proportions, say under 5%, with tungsten for use as a filament material in electric lamps: but to the best of my knowledge the amount of thorium metal incorporated in and uniformly alloyed with the tungsten by proceeding according to these prior processes has been very small, not exceeding a fraction of one percent of the weight of the alloy at best; and even this small proportion of metal has been accompanied by substantial and usually predominating and detrimental amounts of thorium oxide. By the method described below, I am able to alloy thorium metal with tungsten or molybdenum, or with alloys of tungsten and molybdenum, in all proportions from say 1% thorium to 99% tungsten, to 1% tungsten to 99% thorium, and even fractional percentages of even thorium or tungsten; and I have demonstrated that this entire series of binary alloys, when free from substantial or harmful proportions of thorium oxid, is ductile and workable, although with varying ease. For example, the alloys containing thorium in proportions up to about 5% are readily workable by hot swaging and hot drawing methods to the extremely fine gauges of wire now required for electron discharge elements in small audion tubes, say .0015 mm. and finer. With larger proportions of thorium the production of these extremely fine wires becomes increasingly difficult, although the larger sizes, as used in power tubes for example, are readily fabricated. I have also demonstrated that the entire binary series molybdenum-thorium is similarly ductile and workable, and in fact, with even greater facility than the tungsten-thorium series mentioned above. Similarly I have found that the entire series of ternary alloys tungsten-molybdenum-thorium is ductile and workable. My method as described below is applicable in its several modifications to the production of all of the above mentioned alloys, to wit, the binary series tungsten-thorium and molybdenum-thorium, and the ternary series tungsten-molybdenum-thorium. For convenience I will refer hereinafter to tungsten and molybdenum as "refractory metals of the tungsten group."

My method contemplates the formation of a thorium-hydrogen composition which presumably consists of or contains the heretofore described hydride of thorium, ThH_4; and the decomposition or dissociation of this thorium-hydrogen composition, hereafter for convenience designated thorium hydride, in presence of the refractory metal or metals to be alloyed with thorium. My invention is of course not limited by any theoretical considerations, but it may be assumed that the thorium, at the moment of being set free from the hydride, and under the strongly reducing conditions then existing is in condition to alloy with especial readiness with the tungsten or molybdenum or both; and that the hydrogen, at the moment of being set free from the hydride, is particularly active in cleaning the surfaces of the tungsten and molybdenum and thereby facilitating the union of these metals with the thorium. Whatever the explanation may be, I have demonstrated that under these particular conditions homogeneous alloys containing metallic thorium in any desired or pre-determined proportions, and substantially free from oxids, are readily prepared. To the best of my knowledge thorium alloys of this character have not been made prior to my invention.

Thorium powder of high purity is prepared by electrolysis in accordance with the method described in my prior application, Serial No. 713,299 filed May 14, 1924. As thus pre-

pared it is a steel gray powder which is very readily oxidized. When heated in an atmosphere of pure hydrogen to 650° C. or upward it glows strongly, increases in volume, and becomes bluish-black in color, forming the hydride. At decidedly higher temperatures, about 1100–1450° C. this hydride is decomposed or dissociated yielding the metal and hydrogen. It is this decomposition or dissociation of the hydride which, according to my invention, is effected in presence of the refractory metals tungsten or molybdenum or both of these.

The formation of the hydride may be carried out either in presence or absence of the refractory metal. I will illustrate these two procedures by specific examples, relating respectively to alloys of thorium with tungsten and of thorium with molybdenum; it being understood that my invention is not limited to the particular proportions mentioned in the examples by way of illustration, or to the detail of the manipulation described therein; and further, that each of the procedures is applicable, with suitable modifications, to the manufacture of alloys of either type.

Thorium tungsten alloys

Nine grams of pure thorium, 100 mesh or finer, such as may be prepared by the methods of my prior application, is thoroughly blended with 141 grams of finely powdered tungsten of lamp-filament quality. The mixture is transferred to a suitable die and pressed into a rod of approximately rectangular cross-section about 0.30 x 0.25 x 10 inches, the pressure being 10 or 15 tons per square inch, applied laterally. The rod is placed on a supporting surface of tungsten or molybdenum and heated in hydrogen to about 1300° C.–1450° C. When a temperature of 1000° C.–1100° C. is reached, the rod will be seen to glow slightly, and it will expand and more or less completely disintegrate. I attribute this expansion to the formation of thorium hydride.

As the temperature is further increased, the hydride is decomposed. After heating to 1300° C.–1450° C. for about half an hour, the rod is pushed into a water-cooled portion of the furnace, where it cools rapidly, still in a hydrogen atmosphere.

The more or less disintegrated material is placed in an agate mortar and again reduced to fine powder. It is then again pressed into a rod of the same size but using a pressure of 40 to 50 tons per square inch. The rod is then heated in hydrogen to about 1300° C.–1450° C. as before, but this time it does not disintegrate. When cooled, the rod has considerable strength and may be handled freely.

In the next operation the rod is heated by its own resistance in the manner now used in the preparation of ductile tungsten, and in a furnace such as that designed for making ductile tungsten. The rod is held at its upper end in a water-cooled clamp, and dips at its lower end into a pool of mercury. The furnace is water-jacketed and an atmosphere of hydrogen is maintained in its interior about the rod. The following schedule shows the energy-input at the various stages of the heating in a particular case:

Time	Amperes	Volts
12:26	400	5
27	500	8
28	600	9.5
29	700	11.5
30	800	11.8
31	900	11.8
32	1000	11.8
33	1100	12.5
34	1200	12.3
35	1300	13.0
36	1400	13.7
37	1475	13.9
38	1550	14.3
39	1625	14.9
40	1700	15.4
41	1750	15.8
42	1800	16.2
47	1800	15.9
54	1800	15.5

A rod so treated can be swaged to 30 mils without breakage.

The final energy-imput used in the heating is of importance. It will be noted that after a certain stage in the heating is reached, the voltage across the bar may be gradually reduced without reducing the current. In other words, the energy-input at constant voltage tends to increase. At this stage the voltage is preferably decreased to prevent increase in energy-input, and in the example given the input was slightly decreased at the end. The final input was about 27.9 k.w. In a similar experiment, where the final input was 28.8 k.w., the rod could only be reduced to about 0.125 inches diameter, breaking up when further swaging was attempted; while in an experiment where the final input was 29.9 k.w., the rod could not be swaged and broke up in the first die. Swaging was also impossible when the final input was less than 25 k.w. It is manifestly impossible to prescribe the exact final energy-input which will give the best result with each size of rod, each different proportion of thorium and tungsten, and each particular furnace, but the proper input can readily be determined.

The heating schedule of an alloy containing 10% of thorium was as follows:

Time	Amperes	Volts
4:50	400	2.5
51	500	6
52	600	11.5
5:01	700	14.5
02	800	14.2

Time	Amperes	Volts
03	900	15.3
04	1000	15.8
05	1100	15.9
06	1200	17
07	1300	17.5
08	1400	18.3
09	1450	18.0
10	1500	18.3
11	1550	18.4
12	1600	18.8
13	1650	19.3
14	1700	20
26	1700	20

It will be noted that in this case it was unnecessary to reduce the voltage at the end of the process.

The reason for the failure of the rod to disintegrate during the second heating in hydrogen is not entirely clear. The rod is denser due to the higher pressure used in the second pressing, by reason of which hydrogen does not permeate the rod so readily, and furthermore the thorium and tungsten are probably incipiently alloyed at this stage. It is my present belief that these factors are responsible, at least in part, for the failure of the rod to disintegrate.

Thorium molybdenum alloys

Pure thorium metal powder prepared according to the process of my prior application is heated in an atmosphere of pure hydrogen, preferably to about 800—1100° C. The metal glows and hydrogen is strongly absorbed, a decided increase in volume and a color change from steel gray to bluish-black being noted. The resulting powder is very brittle and readily pulverized. It is thoroughly blended, as by grinding in a mortar or otherwise, with finely powdered molybdenum of quality suitable for the manufacture of ductile molybdenum. The powders may be mixed in any proportions, but for high-emission filaments for audion tubes alloys containing from 0.5 to 5% of thorium metal are now preferred. The blended powder is transferred to a suitable die and compressed into rods under 40—50 tons pressure per square inch. These rods are rather fragile and are supported on slabs of tungsten or molybdenum, which are placed in a resistor-wound furnace of the alundum tube type through which hydrogen of high purity and dryness is passed in excess. A convenient form of tube furnace comprises an external steel jacket and a silica packing, hydrogen being passed not only into the tube but likewise into the jacket surrounding the tube, diffusing thence into the tube and the excess hydrogen being burned at the outlet. The bars are heated to about 1450° C., at which temperature hydrogen is expelled from its combination or association with the thorium, and the thorium metal is thus set free in condition to form an alloy, or at least an incipient alloy with the molybdenum. This operation requires about 15 minutes after which the bars are pushed into the cool zone of the furnace, cooled in the hydrogen atmosphere, and removed when the temperature has fallen approximately to normal.

The bars are now sufficiently strong to endure the subsequent manipulation. They are transferred to a hydrogen treating bottle such as is commonly employed in the manufacture of ductile tungsten, and heated therein by their own resistance to a point close to the melting point, and thereafter cooled in hydrogen. In practice I employ at the final stage of the heating a current which is approximately 90% of that which is experimentally determined to be necessary to melt a test bar of the alloy. The thoroughly sintered bar is then reduced to wire of the desired diameter in accordance with the well-known hot swaging and hot drawing operations, starting at about 1700° C. and reducing the temperature with reduction of size of the wire. For the specific purpose of high-emission filaments for standard audion tubes, I reduce the wire to about 1.5 mils or finer, and mount it in vacuum tubes in accordance with the usual practice.

These molybdenum-thorium alloys present certain decided advantages, both in their manufacture and in their subsequent use. They are drawn to wire of very fine size much more readily than are tungsten-thorium alloys of like thorium content. Further, the molybdenum-thorium alloys possess a distinctly higher electron-emission than do tungsten-thorium alloys containing the same proportions of thorium. The reasons for this are still under investigation. While I do not desire to limit my invention by reference to theoretical considerations, it may be stated that it now appears probable that the observed superiority of the molybdenum-thorium alloys, as regards electron-emission, as compared with the tungsten-thorium alloys, results in part at least from a higher rate of diffusion of thorium in molybdenum, whereby the surface requirements of the filaments for thorium are more promptly and effectively supplied.

As advantageous characteristic possessed by both the molybdenum thorium alloys and the tungsten-thorium alloys described above, and possessed also by the ternary alloys mentioned below, is that they do not require the high temperature activation treatment which is necessary for filaments of the known tungsten-thorium oxid type. This characteristic is especially noticeable in the case of molybdenum-thorium and molybdenum-tungsten-thorium alloys. In the case of tungsten-thorium alloys, the initial emissivity may in certain cases be rather low, but in such event it can be normalized and brought to a uniform and high value by operating for a time at a somewhat higher temperature than normal,

although much below the temperatures required for the so-called activition of the filaments of the tungsten-thorium oxid type.

Molybdenum-tungstem-thorium alloys

These are prepared in accordance with either of the modifications mentioned above, that is to say, the hydride of thorium being formed either in presence or absence of the refractory metal, and being thereafter dissociated in presence of refractory metal. Such alloys may be made in all proportions, my present preference being for proportions of thorium up to about 5%; molybdenum 20—40%; the balance tungsten. My invention is not, however, limited to these particular proportions. The essential advantage of these ternary alloys is that they retain the high and uniform emissive qualities of the molybdenum-thorium alloys, while possessing as compared with these a higher stability and life, presumably due to the lowering of the vapor pressure through the presence of tungsten. In this case, as in the case of the molybdenum-thorium alloys mentioned above, it is regarded as probable that the presence of molybdenum in substantial proportions in the alloy facilitates the diffusion of the thorium, and thereby improves the electron-emissivity of the alloy.

The expression "substantially free from oxids" as used herein is intended to indicate that the alloy in question does not contain thorium oxid in proportion to interfere to any material extent with its workability; and further that the proportion of thorium in oxid form is not in excess of the proportion of thorium in the form of metal—or in other words that the preponderating proportion of the thorium content of the alloy is in the reduced condition. So far as I am aware this result has not been before attained in any alloy of thorium with a refractory metal of the tungsten group.

This application is a continuation in part of prior application Serial No. 747,674 filed November 3, 1924, Alloys of tungsten and thorium.

I claim:

1. In a method of making ductile and substantially oxid-free alloys of thorium with a refractory metal or metals of the tungsten group, the steps comprising preparing an intimate mixture of thorium hydride with such refractory metal; subjecting said mixture in compact form to a temperature sufficient to dissociated the hydride; and further heating the product to complete formation of the alloy; the formation of the hydride preceding the compacting of the mixture into a workable body.

2. In a method of making ductile and substantially oxid-free alloys of thorium with a refractory metal or metals of the tungsten group, the steps comprising heating thorium metal in an atmosphere of hydrogen to the temperature of formation of thorium hydride; preparing an intimate mixture of said thorium hydride with such refractory metal or metals; subjecting said mixture in compact form to a temperature sufficient to dissociate the hydride; and further heating the product to complete formation of the alloy.

3. In a method of making ductile and substantially oxid-free alloys of thorium with a refractory metal or metals of the tungsten group, the steps comprising preparing an intimate mixture of thorium hydride with such refractory metal; subjecting said mixture in compact form to a temperature sufficient to dissociate the hydride; and further heating the product by means of its own electrical resistance according to an approximately predetermined schedule, to complete the formation of the alloy.

4. In a method of making ductile and substantially oxid-free alloys of thorium with a refractory metal or metals of the tungsten group, the steps comprising preparing an intimate mixture of thorium hydride with such refractory metal; subjecting said mixture in compact form to a temperature sufficient to dissociate the hydride; and completing the formation of a homogeneous ductile alloy by mechanical working at a high temperature.

5. In a method of making ductile and substantially oxid-free alloys of thorium with a plurality of metals of the tungsten group, the steps comprising preparing an intimate mixture of thorium hydride with such refractory metals; subjecting said mixture in compact form to a temperature sufficient to dissociate the hydride; and further heating the product to complete formation of the alloy; the formation of the hydride preceding the compacting of the mixture into a workable body.

6. In a method of making ductile and substantially oxid-free alloys of thorium with a refractory metal or metals of the tungsten group, the steps comprising preparing an intimate mixture, in powder form, of thorium hydride with such refractory metal; compacting said mixture and subjecting it to a temperature sufficient to dissociate the hydride; and further heating the product to complete formation of the alloy.

7. Process of preparing malleable alloys of tungsten and thorium which consists in blending the pure metal powders in the desired proportions, compressing the mixture, heating the product in hydrogen to about 1400° C., pulverizing, pressing into rods or the like under higher pressure, reheating in hydrogen to about 1400° C., and then heating to a point approximating the melting point to effect complete alloying.

8. The process of making tungsten-thorium alloys which comprises the steps of heating thorium in hydrogen until hydrogena-

tion occurs; compressing into a compact body a mixture containing thorium thus prepared and tungsten; and sintering said body to alloyage; the process comprising also the step of decomposing thorium hydride in intimate contact with tungsten.

In testimony whereof, I affix my signature.

HUGH S. COOPER.