This invention relates to the art of precipitating metals by thermal decomposition of a compound thereof and more particularly to a new and improved apparatus for mounting the filament or starting wire which plays an essential role in the precipitation process. For purposes of illustration, the invention is described herein as being of especial utility in the thermal decomposition of zirconium iodide for the production of a deposit of zirconium crystal bar having the characteristics of improved ductility, corrosion resistance and high purity. However, as will later become apparent the invention is in no way limited to this single example but on the contrary is intended for use in the preparation of many other metals or alloys, as for example the preparation of titanium, vanadium, hafnium and the like.

Certain special requirements are to be found in apparatus employing "hot-wire" techniques of metal deposition although the combination of apparatus in itself is comparatively simple. For example, the entire exposed filament or starting wire, along with the metal deposited thereon, must at all times remain at a temperature above the decomposition temperature of the decomposable compound, which in the case of zirconium iodide is about 1300-1500°C. Depending upon the type of crystal growth desired in the deposited material. In order to maintain this temperature the amount of current supplied to the wire and its deposit continues to increase as the deposit grows. As a consequence, the likelihood of considerable heat being conducted away from the ends of the hot wire and its deposit to the electrode, or to an intermediate element between the electrode and hot wire, is thus enhanced. However, if excessive heat flow thus takes place at the ends of the hot wire the wire may fall below the decomposition temperature at that point, whereupon the gas liberated from the decomposable compound, in the illustrative example, iodine, will then attack the deposit at this cooler end of the wire. In a short time the wire at this point will start to fuse since as more current is supplied to maintain the decomposition temperature at the other parts of the wire and its deposit, this particular cooled portion of the wire will have insufficient current carrying capacity.

A further requirement is that the filament arrangement must permit of the deposit of sufficient material at its ends as well as along the filament, to carry a very high current especially at the latter stages of growth of the deposit.

Furthermore, in view of the desirability of maximum efficiency of both the vacuum apparatus and the means employed for heating the metal compound to its vaporization temperature prior to the decomposition step, as well as the advantages resulting from production of large diameter bars of deposited material, a requirement exists for apparatus which can consistently produce bars of one inch diameter or larger. To illustrate the problem involved in preparing this size of bar it will be noted that a current of approximately 1800 amperes is needed to maintain a one inch diameter bar at a temperature sufficient to decompose zirconium iodide vapor on the outer surface thereof.

In addition, a further requirement resides in providing a suitable mechanical mounting to withstand the weight of the heavy bar deposit and without compromising the solution already provided by the invention for the other requirements.

Still another requirement is the provision of a combination of apparatus in which suitable maintenance of the electrodes and ready attachment or detachment of the filament and deposited bar thereto or therefrom can be readily carried out.

Accordingly, the present invention has as an object the provision of a new and improved apparatus for solving the above-mentioned requirements in the art of precipitation of metals by thermal decomposition methods.

Other objects and advantages of the invention will become apparent when considered in connection with the following description and the accompanying drawings wherein,

Figure 1 is a view, partly in section, showing a vessel in which thermal decomposition of a metal compound for hot wire deposition of the metal may be carried out using the improved apparatus of my invention.

Figure 2 is an elevation view of one form of improved hot-wire tip embodying the invention. Figure 3 is a top plan view of the tip shown in Figure 2.

Figure 4 is a sectional elevation view of the tip shown in Figure 2 and showing one arrangement for mounting a starting wire upon the tip.

Figure 5 is a sectional elevation view of the tip shown in Figure 2 and showing a second arrangement for mounting a starting wire upon the tip.

Referring now to Figure 1, a suitable vessel or reaction chamber 10, having an associated heating means 11, is provided for containing the vapor of the metal compound. A conduit 12 leading to an evacuating means and a flanged
lid 13 of the vessel preferably are employed to the end that a desired metal compound may be dissolved, and concentrating all may thereafter be drawn out of said vessel prior to the formation of the vapor resulting from external applied heat, all in the manner known in the art. As will be apparent to those skilled in this work, certain standard precautions will be necessary in carrying out the process, especially in view of the highly corrosive nature of the liberated gas evolved from the metal compound. The material used in construction of vessel 10 and other exposed apparatus will accordingly be selected with this feature in mind. For example in the cyclode iodide process of preparing ductile zirconium, the zirconium to be deposited together with a small amount of iodine or zirconium iodide may be loaded into vessel 10, or into a cracking bottle which can be broken after being enclosed in the vessel. After suitable evacuation of the vessel the heating means 11 may be operated to cause a zirconium iodide vapor to permeate the vessel. Thereafter the hot-wire filament, later to be described, is raised to a suitable temperature and the volatile zirconium tetrailodide will decompose on that wire leaving a deposit of elementary zirconium and liberating the elemental iodine. This iodine in turn diffuses back to the crude zirconium material, forms more of the metal iodide which in turn diffuses to the wire and is decomposed. In this way the seed filament or wire has built upon it a heavy deposit of zirconium resulting it can be supported on the electrodes and can constantly receive enough current to remain above the decomposition temperature of the metal compound vapor.

For carrying out this type of process there is mounted within the lid 13 two massive electrodes 14 and 15 suitably insulated from the vessel and having heavy leads 16 and 17 respectively connected thereto. These leads which may be called upon to carry currents in the order of 2000 amperes or greater, are suitably connected to a remote source of electrical current permitting an appropriate increase in the flow of current as the deposited metal increases within the vessel, thereby to permit the maintenance of such deposited metal at an appropriate temperature. A starting wire or filament 25, also known as a "hot-wire" is suspended within the space of the vessel and in accordance with my invention is connected at its ends to the respective electrodes by means of the detachable electrode tips 21 and 22. This wire preferably is of a small diameter, in one instance of satisfactory usage being 0.008 inch diameter, and may be either of the same material as the metal to be deposited, or of a different material than the metal to be deposited as whenever an alloyed final product is permissible. As shown in Figures 2 and 3, a preferred form of electrode tip may consist of a tapered solid metal member having an enlarged head portion 21 and a reduced tail portion 22 and with a centrally disposed aperture 23 therethrough. The enlarged head portion is adapted to contact the electrode with a large surface of contact thus permitting an efficient flow of heat by conduction when large electric currents are passing through the assembly. The tapered tail portion preferably terminates in a reduced outside diameter which is less than twice the diameter of the starting wire or of the aperture 23 through which such wire may be passed. In this way the conduction of heat from the wire to the tip at this critical point of connection is limited and no appreciable cooling of the wire at this point can take place. While the outside diameter of the wire is variable in accordance with the type of material employed and should not exceed twice the diameter of the wire I have actually found that better results are assured when its diameter actually approaches that of the wire. For example, in using a wire of 0.06 inch diameter an outside diameter of about 0.10 to 0.13 inch has been found to give excellent results. Also, in order to insure a good mechanical support for the deposit of heavy metal upon the wire, means are provided for a rigid but detachable mounting of the electrode tip upon such electrodes of means which has proven satisfactory consists of a plurality of adjustable set screws 24 adapted to pass through the lower portion of the electrode and engage with a circumferential groove 25 contained on the periphery of the enlarged head of the tip member. Other means of detachably connecting the electrode tip to the electrode however may be used as desired without departing from the invention.

In order to connect the starting wire to the tip various arrangements may be employed provided the conduction of heat from the wire to the tip is suitably limited. For example, as shown in Figure 5, a looped wire 30 may be positioned within aperture 23 with its ends 31 and 32 anchored into suitable grooves at the top of the tip head and with the closed loop end of the connector extending a short distance outwardly of the tail of the electrode tip. Starting wire 25 may then be joined to the connector by having the loop 33 pass through a small hole in the end of the wire, by use of a small separate ring, or by other equivalent means.

In an alternate arrangement shown in Figure 5 the starting wire 25 may be positioned in aperture 23 and the end 41 thereof may be anchored in a groove at the head of the tip. With the apparatus employed as above described the process of depositing metal may then be carried out without being subject to the disadvantages common to the previous practices. For example, as the wire 13 becomes filled with a vapor of the metallic compound and the hot wire 25 is heated above the decomposition temperature of that vapor, the metal starts to deposit on all of the surface of the hot wire and a rod-like bar of deposited metal starts to grow. The junction of the wire and the tail of the electrode tip is soon covered with such deposit and as the process continues this deposit progressively forms along the tapered tail portion of the tip thus providing an increased current carrying deposit. Through leads 16 and 17 a constantly increasing supply of current is supplied in order to keep the entire deposit of metal at a temperature above the decomposition temperature and the heat thus created may flow to the electrodes through the larger areas provided by the head of the tapered tips. Too possibility of the end of the hot wire thus becoming fused and melted away due to carrying too much heat at any stage of the process is thus eliminated.

It has been found that refractory metals such as molybdenum, tantalum, titanium, tungsten, zirconium, hafnium and the like, as well as graphite, are especially suited for use in forming the tip. In general, any refractory metal which does not alloy with the metal being deposited at the temperature of deposition may be employed. If desired the entire tip may be made of the same material...
as that composing the starting wire 20, or as that of the metal being deposited, or both.

After the deposited bar of metal has been grown to the desired size the heater 11 may be disconnected, the supply of current to the electrodes may be discontinued and the lid 13 of the vessel may be removed. Normally, the gas, such as iodine, will at this time be deposited as a solid upon cooler portions of the vessel. By loosening screws 24 the tips and metal deposit may be disconnected from the apparatus and removed for further processing, while a new wire and tip may be replaced on the electrodes, a new charge of material may be added to the vessel, and the lid replaced upon the vessel for a subsequent cycle of metal deposition.

Various changes in construction and materials of the tips and attached wire may be made without departing from the scope of the invention and it is not desired to limit my invention to the exact details as shown except insofar as defined in the following claims.

What is claimed is:

1. In combination, a vessel adapted to contain a thermally decomposable vapor of a metal compound, electrodes having a cavity in the end thereof mounted within said vessel, a starting wire adapted to be maintained at a temperature above the decomposing temperature of said vapor by a current supplied to said electrodes, and demountable electrode tip means for attaching the ends of said wire to said electrodes, said means comprising an enlarged head portion adapted to be mounted in the electrode cavity and having a recessed surface, a tail portion having a diameter not more than twice the diameter of said wire, retaining means adapted to engage the electrode and the recessed surface and an intermediate tapered tip portion connecting said head and tail portions to provide said means with a tapered configuration with the point of wire attachment thereto being at the tail portion of said means, thereby to insure the maintenance of the temperature at the ends of said wire above said decomposing temperature by limiting the flow of heat by conduction from the ends of the hot wire to the adjacent electrodes.

2. A tapered electrode tip suitable for detachable mounting upon a cooperating electrode and having a head portion of relatively large heat conducting capacity and diameter and a tail portion of relatively small heat conducting capacity and diameter, said portions being provided with an aperture extending centrally therethrough and adapted to house the mounting means for a relatively small hot wire filament the head portion having a recessed surface for use with a separate detachable fastening means engageable in the electrode and recess.

3. An article as defined in claim 2, wherein said head portion is provided with means for anchoring the end of a hot wire filament extending through said aperture from the open end of said tail portion.

4. An article as defined in claim 2 wherein said head portion includes means for anchoring a separate connector extending through said aperture from the open end of said tail portion and connected to the end of a filament at a point spaced from said tail portion.

5. A tapered electrode tip suitable for detachable mounting upon a cooperating electrode and being composed of a refractory metal and having a head portion of relatively large heat conducting capacity and diameter and a tail portion of relatively small heat conducting capacity and diameter, said portions being provided with an aperture extending centrally therethrough and adapted to house the mounting means for a relatively small hot wire filament whose diameter is not more than one-half the diameter of said tail portion, the head portion having a recessed surface for use with a separate detachable fastening means engageable in the electrode and recess.

6. An article as defined in claim 5, wherein said tip consists of molybdenum.

7. An article as defined in claim 5, wherein said tip consists of tantalum.

8. An article as defined in claim 5, wherein said tip consists of tungsten.

9. An article as defined in claim 5, wherein said tip consists of zirconium.

10. An article as defined in claim 5, wherein said tip consists of hafnium.

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