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Sleppy et al.

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[54] **PROCESS FOR ELECTROLYTIC RECOVERY OF METALLIC GALLIUM**

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[52] **U.S. Cl.**..... **204/105 R**; 423/158; 423/602

[51] **Int. Cl.**..... **C25c 1/22**

[58] **Field of Search**..... 204/105 R; 423/158, 602

[56] **References Cited**

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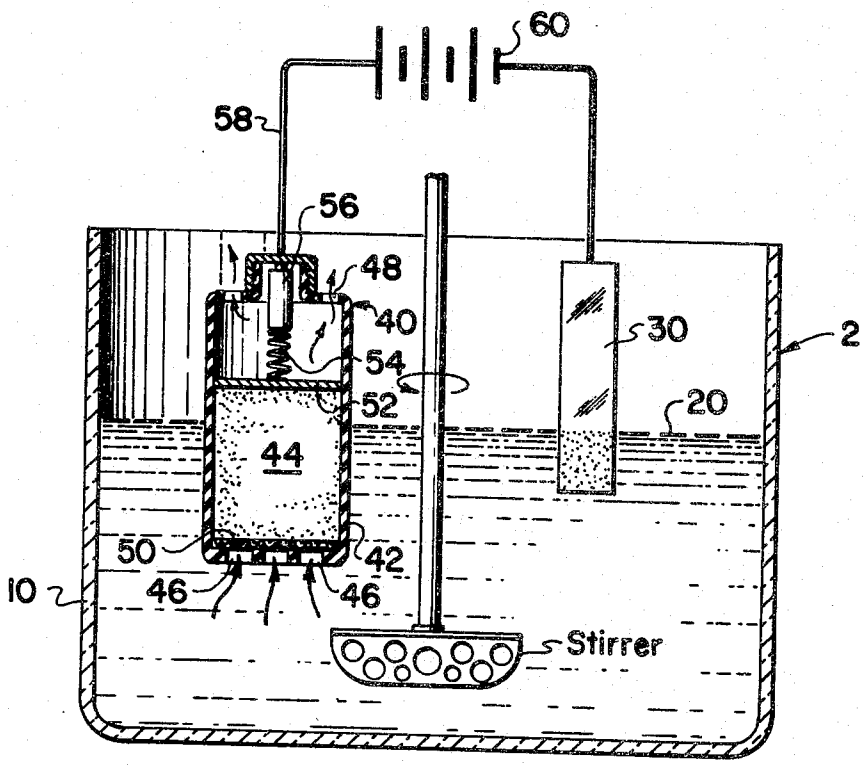
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[57] **ABSTRACT**

Gallium metal is electrolytically extracted from gallium compounds by a process which simultaneously dissolves the compound and reduces the metal.

9 Claims, 3 Drawing Figures



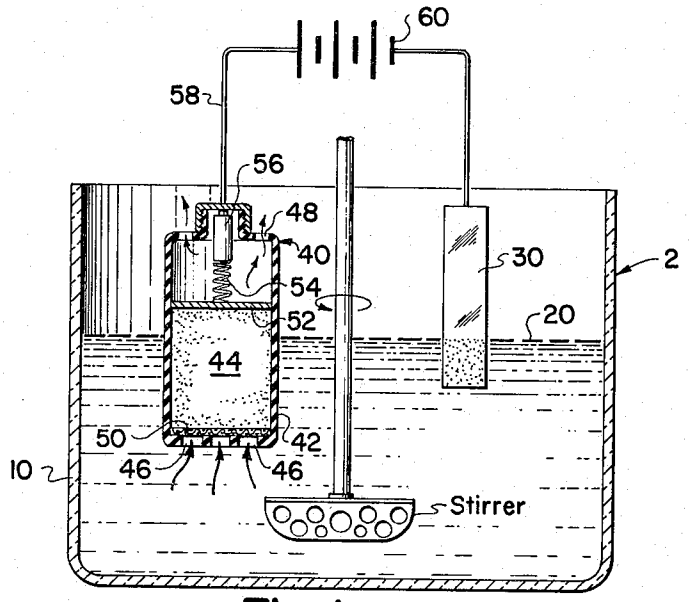


Fig. 1

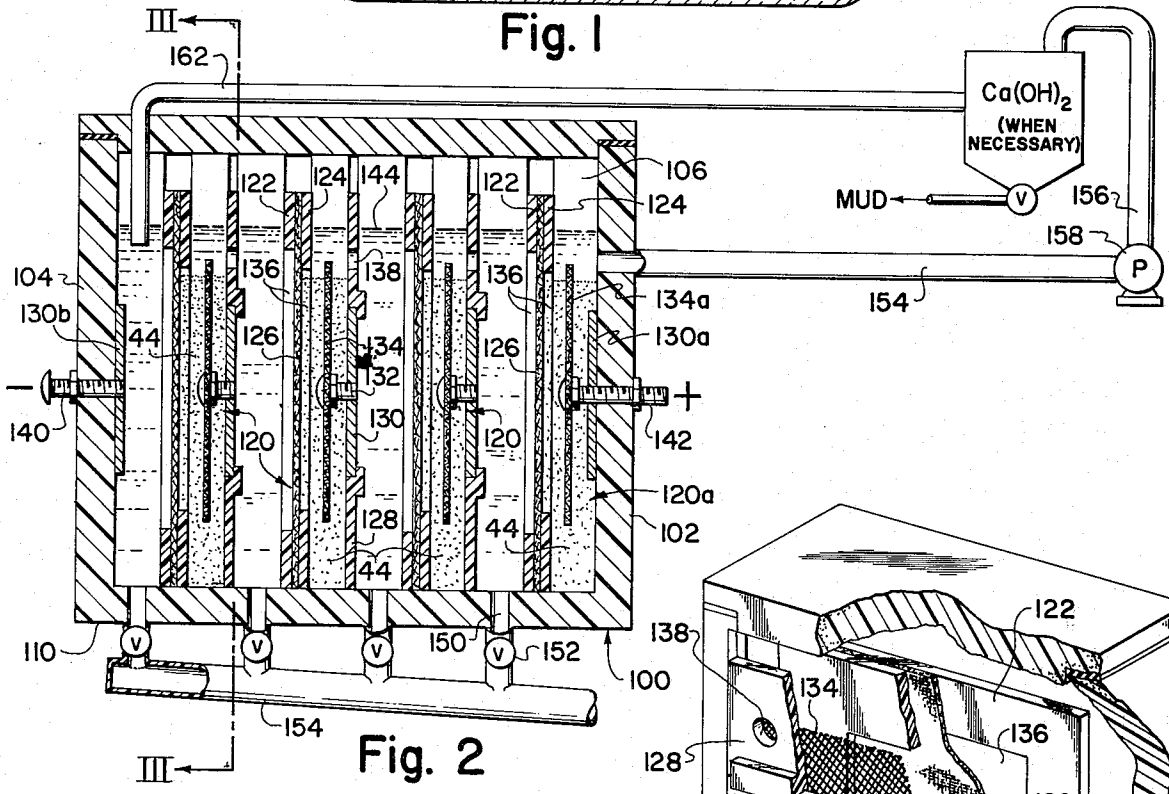


Fig. 2

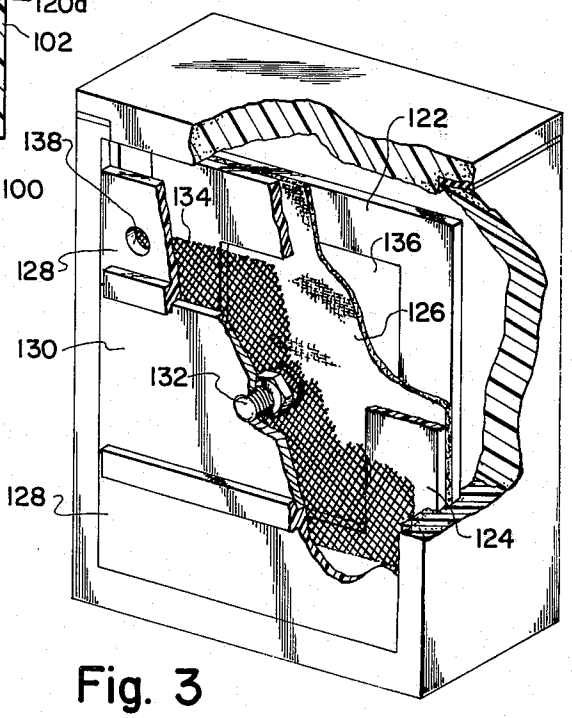


Fig. 3

PROCESS FOR ELECTROLYTIC RECOVERY OF METALLIC GALLIUM

BACKGROUND OF THE INVENTION

This invention relates to the electrolytic production of gallium metal. More particularly, the invention relates to the electrolytic production of metallic gallium directly from a gallium compound which comprises one electrode of the electrolytic cell.

The demand for gallium metal is rapidly expanding due, at least in part, to its use in the electronics industry in applications such as light emitting diodes and microwave cavity devices. The manufacturing processes for such devices generate much scrap in the form of gallium compounds such as GaAs, GaP, and GaAsP.

The reclamation of metallic gallium from these compounds is complicated by the insolubility of the compounds in conventional solvents. Because of this insolubility, gallium compounds are conventionally recycled to recover the gallium by processes which require a large amount of energy in the form of heat. For example, gallium may be recovered from gallium arsenide (GaAs) by volatilization of arsenide vapors as As_4. However, this requires a temperature of at least 1,200°C as well as a dry and oxygen-free system.

In an alternate system, the gallium compound is dry fused with a base such as NaOH at 450°C to convert the gallium into sodium gallate which can then be dissolved in an aqueous basic solvent such as NaOH prior to subsequent electrolytic reduction of the gallium metal.

In view of the rising costs of energy and the desire for conservation of available energy, it would be desirable to eliminate the need for conversion—via heat—of insoluble gallium compounds into more soluble forms.

SUMMARY OF THE INVENTION

Quite surprisingly, it has now been discovered that gallium compounds may be dissolved electrolytically in the same cell used for reduction of gallium metal by making the solid gallium compound the anode of the cell. In a preferred embodiment, the undissolved compound is present in particulate form and is contained in an electrolytically permeable holder which may also have conductive means therein relatively inert to the electrolytic process.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a diagrammatic cross sectional view of a cell illustrating the invention.

FIG. 2 is a cross sectional view of a multi-electrode bipolar cell constructed in accordance with the invention.

FIG. 3 is a partially broken away end view of one of the bipolar electrode assemblies shown in FIG. 2.

DETAILED DESCRIPTION

Referring now to FIG. 1, a simple two-electrode cell is illustrated at 2 comprising a container 10 with an aqueous electrolyte 20 such as NaOH therein. A metal cathode 30 which preferably is constructed of stainless steel, nickel, or other suitable material chemically inert to the electrolyte is at least partially immersed in the electrolyte.

The gallium compound to be dissolved and reduced to metallic gallium in accordance with the invention is contained in an anode assembly 40 which is also immersed in electrolyte 20. Anode assembly 40 comprises

a non-conductive hollow container 42 made of glass or plastic or the like in which the gallium compound may be placed in particulate form as shown at 44.

Container 42 is provided with holes 46 and holes 48 to respectively permit entrance of electrolyte and exiting of generated gases. Filter paper or cloth or other chemically inert permeable membrane 50 is placed over holes 46 to prevent loss of particulate gallium compound while permitting access to the gallium compound by the electrolyte.

Electrical contact with the gallium compound is maintained in the illustrated embodiment of FIG. 1 via a plate 52 which may be stainless steel or nickel or other chemically inert conductor such as graphite and which is biased against the gallium compound particles by a spring 54 which also provides electrical contact to a terminal 56 which is suitably mounted on container 42.

A lead 58 connected to terminal 56 provides mechanical support for anode assembly 40 as well as electrical connection to a suitable DC power source illustrated in FIG. 1 as a battery 60.

In operation, a gallium compound such as GaAs is ground to a particle size of about −10 to +48 mesh and placed in anode assembly 40 in cell 2. After electrical connection with DC power source 60, the anodically polarized GaAs dissolves into and reacts with the electrolyte to form dissolved and hydrolyzed gallate and arsenite ions. Simultaneous electrolysis of H_2O causing evolution of H_2 at the cathode and O_2 at the anode accompanies the anodic dissolution of the gallium compound. The gallium containing ions, upon reaching cathode 30, are reduced to gallium metal. Arsenite is built up in the bath as dissolved AsO_2^- which gradually oxidizes to AsO_4^{-3} until the solubility of $Na_3AsO_4.12H_2O$ is exceeded.

To avoid precipitation of the hydrated sodium arsenate salt, the electrolyte must be changed or treated in an appropriate manner to remove arsenate. In a preferred embodiment, electrolyte is continuously pumped from the cell into a reaction vessel for treatment with lime to precipitate an insoluble calcium arsenate as $Ca_3(AsO_4)_2$. The purified and regenerated electrolyte is then circulated back to the cell.

While the gallium compound has been illustrated in its preferred form as particulate, a solid gallium compound anode could be used. However, the use of the compound in particulate form increases the surface area thus increasing dissolution and current efficiency with respect to cathodic deposition of gallium. Furthermore, it has been found that, when solid anodes are used, minor amounts of the salt—in undissolved form—may "dust" off the anode and migrate to the cathode to, in effect, poison it. This latter effect can, of course, be minimized by the isolation of the anode from the cathode with filter cloth as previously described in connection with the description of anode assembly 40.

It has been further noted that the cathode should preferably be conditioned by an initial plating of gallium thereon. This can most advantageously be accomplished by adding a minor amount of dissolved gallium to the electrolyte prior to start-up of the cell. This will permit a sufficient initial deposition of gallium on the cathode prior to build-up of gallium ions in the bath due to dissolution of the gallium salt.

Turning now to FIG. 2, another embodiment is illustrated wherein the invention is carried out using bipolar

electrode assemblies. A non-conductive housing **100** comprises sidewalls **102** and **104**, backwall **106**, a front wall (not shown) and a bottom portion **110**.

Within housing **100** and supported by bottom portion **110** are a plurality of bipolar electrode assemblies **120**. Electrode assembly **120** comprises non-conductive frame portions **122** and **124** between which is sandwiched a filter cloth **126** which together form one wall of the electrode assembly. A satisfactory filter cloth is No. **219** monofilament nylon weighing **150** grams/m^2 with about **50** filaments per cm. Other materials can be substituted provided that they possess satisfactory chemical inertness, and are sufficiently fine so as to contain the particulate salt. Another non-conductive wall member **128** is spaced therefrom having mounted thereon a stainless steel electrode **130**. A metallic stud member **132** passes through member **128** and electrode **130** and carries a second electrode **134** which may be a metallic plate or screen which is positioned parallel to and approximately midway between frame member **124** and wall member **128**.

Frame members **122** and **124** and wall member **128** extend from back wall **106** of container **102** to the front wall to form a reservoir or chamber with stud member **132** protruding therein and positioning electrode **134** in the approximate center of the chamber. The chamber is filled with a gallium compound **44** such as GaAs in particulate form of preferably about −**10** to +**48** mesh. The gallium compound comprises the anode of each bipolar electrode assembly while electrode **130** comprises the cathode. Electrical connection therebetween is maintained via stud **132** and electrode **134**.

An electrode **130***b* is mounted on wall **104** via a threaded bolt **140** which passes through wall **104** and provides an external terminal for connection to the negative side of a DC source of power (not shown). This electrode comprises the cathode for the anodic portion of the adjacent bipolar electrode.

In similar fashion, electrode assembly **120***a* comprises only an anode with container walls **102** forming one wall of the electrode assembly. Electrode **134***a* is centrally positioned within electrode assembly **120***a* by a threaded bolt **142** which replaced stud **132** and which passes through container wall **102** to provide a positive terminal for connection to the positive side of the DC source of power. An electrode **130***a* is provided not to act as cathode in this case, but to provide total area of contact between the gallium compound and electrode **134***a* and **130***a* equivalent to the contact area in the other bipolar electrodes.

After assembly of the electrodes, including placement of the gallium compound therein, the container is filled with an electrolyte **144** which is preferably a base such as NaOH at a concentration of about **100** to **200** grams per liter (expressed as equivalent Na_2CO_3). The electrolyte level is sufficiently high to provide direct communication with the interior of each bipolar electrode through holes **136** in frame members **122** and **124** and holes **138** in wall member **128**. Holes **136** and **138** are respectively positioned to be above the level of gallium compound but below the electrolyte level. This permits circulation of the dissolved salt to maintain a constant concentration in the cell. The size of the holes is selected to allow only about **1%** current leakage.

The bipolar cell is operated at a temperature above room temperature and preferably at a temperature of about **70°** to **90°C** to increase efficiency. This temperature is well above the melting point of metallic gallium and thus the gallium, as it deposits on the cathode **130**, drops to the bottom of the cell. In this manner the gallium may be collected through openings **150** provided in bottom portion **110** of the cell. Each opening is provided with a valve **152** which controls the flow to a common collection trough **154**.

As previously stated, the reduction of gallium is accompanied by an oxidation of the arsenic ion to an arsenite (AsO_2^-) which gradually oxides further to arsenate (AsO_4^{-3}). The arsenate ion content will gradually build up until the solubility of Na_3AsO_4 is exceeded. While the elevated operating temperature permits accumulation of greater amounts of arsenate, it eventually becomes necessary to remove some of the arsenate ions.

In the illustrated embodiment of FIG. **2** this is accomplished by continuously pumping a portion of electrolyte **144** into a reaction vessel **160** via pipes **154** and **156** and a pump **158**. The arsenate-laden electrolyte is treated with an hydroxide such as calcium hydroxide or magnesium hydroxide which will precipitate the arsenate. The precipitate (such as calcium arsenate) settles in the reactor while the thus-purified and regenerated electrolyte is then returned to the cell via a pipe **162**.

By providing appropriate hopper feed bins for each electrode assembly, it is possible to provide a continuously operating cell wherein gallium compound is added to the electrodes and gallium metal and the anionic portion of the initial gallium compound are both continuously removed.

Each compartment optionally operates at about **4** to **5** volts with optimum current densities of about **15** to **20** amps/dm^2 on the cathode and **10** to **15** amps/dm^2 on the anode.

In actual use using **3** electrode assemblies, each having **9,450** cm^3 volume, a total voltage of **24.8** and a total current of **133** Ampere hours, **0.94** grams of gallium were produced per hour for a period of **18.8** hours. During this period of operation, periodic additions of gallium arsenide were made to each electrode assembly and the spent electrolyte was circulated through an external vessel for periodic treatment with lime. The current efficiency, i.e., that portion of the total current flow which resulted in reduction of gallium into metallic form, was calculated to be **5.1%** per electrode assembly or **15.3%** for the entire cell.

Thus my invention provides for electrolytic dissolution of insoluble gallium compounds while permitting simultaneous electrolytic reduction of gallium metal. In the preferred embodiment, my invention may be practiced on a continuous basis using bipolar electrodes.

While the invention has been described with respect to certain illustrated embodiments, it will be readily appreciated that minor modifications may be made while not departing from the spirit of the invention.

What is claimed is:

1. A process for the recovery of gallium metal from gallium compounds which comprises:

a. establishing the gallium compound as a dissolvable anode in an electrolytic cell;

b. passing a current between the gallium compound anode and an inert cathode to effect anodic dissolution of the gallium compound; and

c. simultaneously plating out metallic gallium on said cathode.

2. The process of claim 1 wherein the gallium compound comprises gallium arsenide and the amount of dissolved arsenate ion is controlled by removal of a portion of said electrolyte and treating said electrolyte with a material which will cause precipitation of said arsenate.

3. The process of claim 2 wherein a portion of said electrolyte is continuously circulated from said cell into a reaction zone to precipitate arsenate therefrom.

4. The process of claim 3 wherein said arsenate-containing electrolyte is treated with lime to precipitate calcium arsenate from said electrolyte.

5. The process of claim 1 wherein said electrolytic cell contains an aqueous alkaline solution.

6. The process of claim 5 wherein said aqueous alkaline solution contains at least 1 gram per liter of dissolved gallium prior to start-up of the cell to provide conditioning of the cathode by providing deposition of a smooth clean liquid gallium coating on the cathode contemporaneous with the initial dissolution of the gallium compound anode.

7. The process of claim 1 wherein said gallium compound anode is in particulate form.

8. The process of claim 7 wherein said particulate gallium compound is contained in an electrolytically permeable holder.

9. The process of claim 1 wherein said electrolytic cell comprises a plurality of bipolar cells in series.

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