March 20, 1973 G. K. JONES **3,721,611**

PROCESS FOR THE PRODUCTION OF METALS

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Fig. 1.

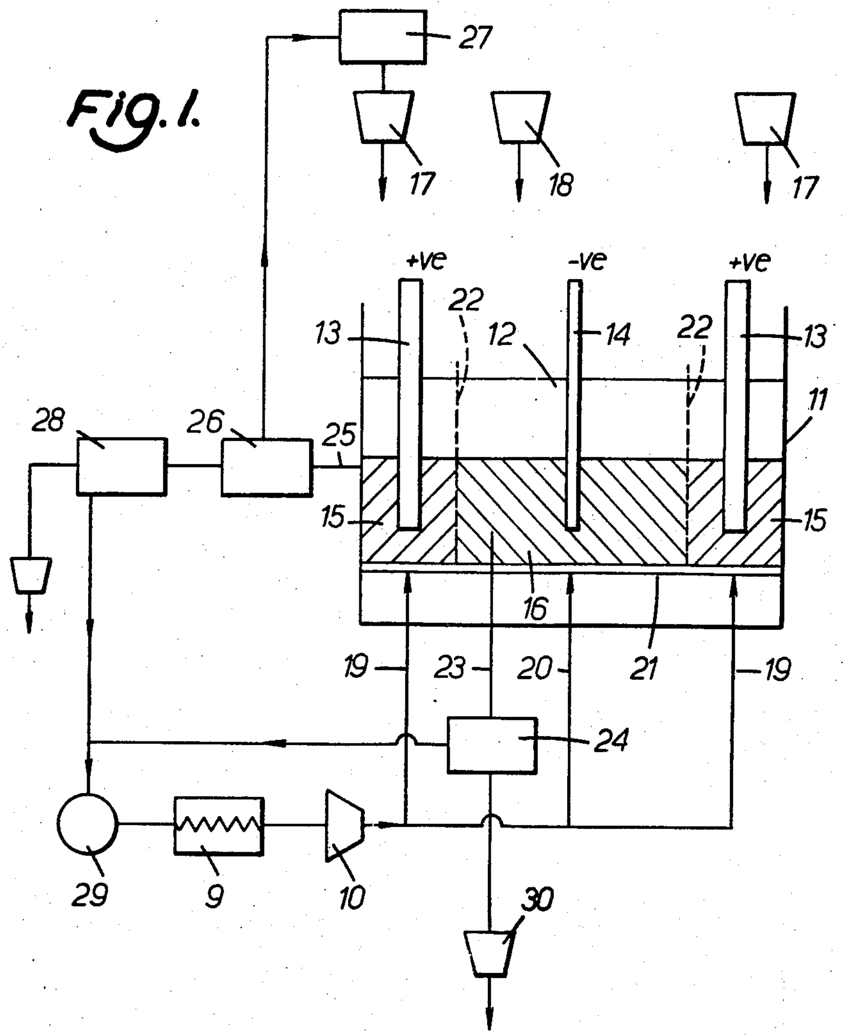
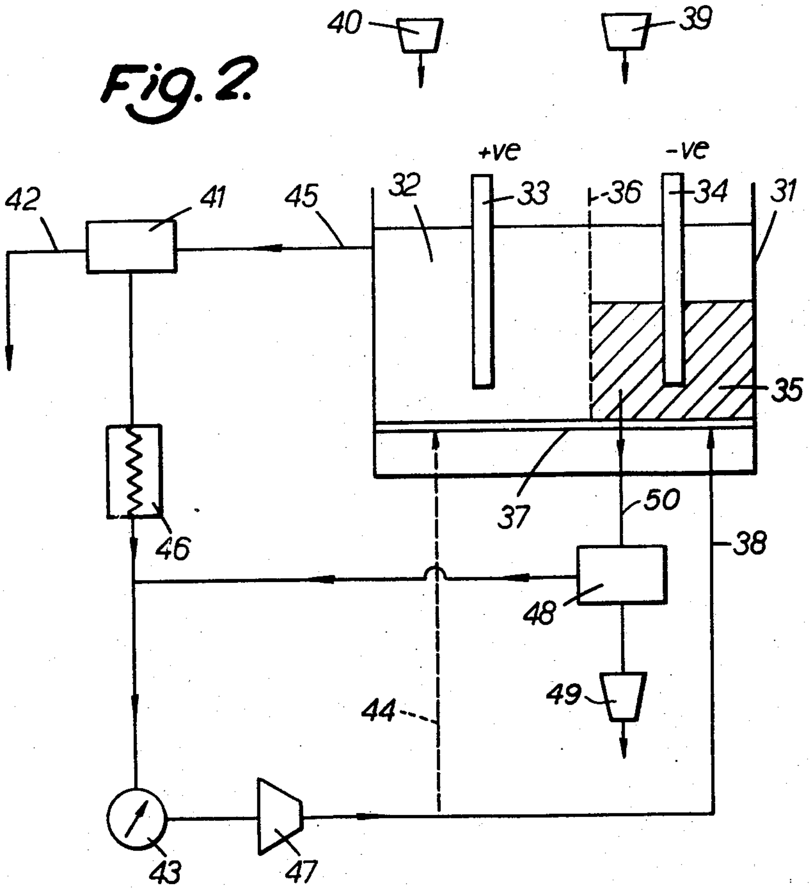


Fig. 2.



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PROCESS FOR THE PRODUCTION OF METALS

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U.S. Cl. 204—1 R 9 Claims

ABSTRACT OF THE DISCLOSURE

A process for the electrodeposition of metal comprises passing an electric current through a cell containing a cathode consisting of a bed of conducting particles of the metal to be recovered fluidized by passing the electrolyte therethrough and supplied with current by a stationary conducting member in electrical contact therewith, the conducting member forming a portion of the total cathode area.

The present invention relates to a process for the production of metals, and in particular to an electrodeposition process.

Electrolytic processes for the purification of metals such as copper, tin, manganese, indium and several of the precious metals are well known. These processes commonly employ conventional electrochemical cells in which ingots of partly refined metal form the anodes and at the start of the process the cathodes are formed of a relatively small bulk of pure metal. The electrolyte usually consists of an aqueous solution of a pure salt of the metal so formulated as to promote its electrodeposition on the cathodes in a desired form and purity at a high current efficiency.

Such processes have two main inherent disadvantages. Firstly, they are essentially batch processes in which after a certain period it becomes necesary to shut down and remove the cathodes on account of their excessive bulk, to install fresh anodes, and to purify the electrolyte by filtration and/or removal of soluble impurities arising from the anode material. Secondly, the volume output of such processes is exceedingly low in proportion to the size of plant required, since high current densities per unit area of cathode cannot usually be employed without adversely affecting the current efficiency and the physical properties of the product.

Attempts have been made to overcome the second of these disadvantages, for example, by arranging for the electrolyte to flow rapidly past the cathode which is gradually retracted to compensate for the increasing thickness of the deposit. In this way much higher rates of deposition can be attained and the process can also be made quasi-continuous. However, the high currents and small clearances involved introduce fresh difficulties of control.

According to the present invention there is provided a process for the production of metals by electrodeposition, which process comprises passing an electric current through a cell containing a cathode, an anode and an electrolyte, the cathode consisting essentially of a bed of small particles of the metal to be recovered fluidized by passing the electrolyte therethrough and supplied with current by a stationary conducting member in electrical contact therewith, the conducting member forming a small part of the total cathode area, and the nature of the anode, the electrolyte and the current density being such that the particles of the bed progressively increase in size through electrodeposition of pure metal thereon. The particles of increased size may be continuously or periodically separated from the bed and replaced by fresh

small particles of metal. This may be achieved by making use of their increasing tendency to settle under gravity, or by the use of other known techniques for separating oversize particles from a suspension.

The process of the invention may be used to purify metals or to produce or recover them (electrowinning). Preferably, if the process is one of metal purification, the particles constituting the cathode consist of pure metal.

If convenient, the anode can be a rod or slab of impure metal or can be an inert anode. Preferably it consists of a bed of conducting particles, preferably metal particles, either at rest or fluidized by the passage of electrolyte therethrough, and supplied with current by a stationary conducting member in contact therewith, the member forming a small part of the total anode area.

Where the anode is consumed during operation of the process, particles of decreased size may be continuously or periodically separated from the anode bed and replaced by fresh particles. The separation may be achieved by the use of known techniques such as screening or hydrocycloning.

The stationary anode and cathode members may be rods or wires of impure or partially refined metal, or they may be inert.

The electrolyte may be aqueous or non-aqueous and may contain the metal in solution in the form of a simple or complex salt.

Where both the cathode and anode consist of fluidized particles it will be necessary to prevent intermingling, contact and consequent short circuiting between the fluidized beds. This may be achieved by the use of one or more porous diaphragms to separate the anode and cathode regions.

Where possible, it is preferred that the particles comprising either or both beds be spherical in shape to promote mutual contact and ease of fluidization.

The particles of the electrode beds may have a mean diameter of from 20μ to 1000μ, preferably from 50μ to 250μ. It will be understood that the more dense the electrode material, the smaller may be the particles. Conveniently each conducting member may form about 1% of the respective total electrode area.

Although it is preferable to have both electrodes in fluidized form, in some instances this may not be convenient, and, in such a case, an inert stationary anode of, for example, carbon or lead may then be suitably employed. This may be the case, for example, in the electrowinning of zinc where the most suitable electrolyte is acid zinc sulphate solution; as the process goes forward deposition of zinc together with discharge of hydroxyl ions and evolution of oxygen at the inert anode will lead to a progressive increase in acidity which can be continuously corrected by the addition of zinc oxide as feed, this being produced by roasting of, for example, a sulphide ore.

On the other hand, in an electrorefining operation where there will in general be a plentiful supply of crude metal, this may be readily available in, or convertible to, finely-divided particulate form and in this case such particles will clearly form the most suitable anode material. Also, the stationary anode and cathode members may conveniently consist of detachable rods or wires of impure metal. These, even if protected from any substantial electrolytic action by a dense surrounding fluidized bed, will tend respectively to decrease and increase in size as the process continues, and may if desired be interchanged from time to time to restore the status quo.

The process of the invention has two substantial advantages over conventional electrorefining and electrowinning techniques. Firstly, it can, if desired, be operated as a continuous process in that it is possible to continuously or periodically replace cathode or cathode and anode particles by fresh particles of standard size, and since the electrolyte is circulated continuously through the system, to continuously monitor and control the electrolyte temperature, pH, metal content and any other desired characteristics.

Secondly, the proces of the invention makes far more economical use of space by presenting a much greater electrode area per unit of volume. For example, in a conventional cell for the electrorefining of copper, a tank of a capacity of about 1,600 cu.ft. may hold about 30 plate cathodes of area not more than about 20 square feet, i.e. an area of less than 2 square feet of cathode per cubic foot of cell volume, giving in practice a copper output of about 6 oz. per day per cubic foot. On the other hand, using as cathode copper spheres of diameter 0.002″, a suitable size for the purpose of this invention, and assuming that half the working cell volume may be alloted to the cathode region, of which half again may contain electrolyte, one-third of the volume of which may be occupied by the fluidized cathode material, it can be calculated that the available cathode area per cubic foot of cell is of the order of 1000 times that of the conventional cell. Even allowing for the fact that, in a fluidized conducting medium, the overall electrical conductivity may be no more than about 30% of that of the same system in a rest state, the possible gain in output per unit volume is obviously very great.

Furthermore, it is practicable, if desired, to operate at a current density much lower than heretofore economically possible, with the consequent advantages of higher current efficiency and improved deposit quality, while retaining high output.

The process of the invention will now be described by way of example with reference to the accompanying drawings in which:

FIG. 1 shows diagrammatically a form of apparatus suitable for use in the electrorefining of copper, and

FIG. 2 shows diagrammatically a form of apparatus suitable for use in the electrowinning of zinc.

Referring to FIG. 1, the cell **11** contains acid copper sulphate electrolyte **12** suitably at a temperature of about 60° C. Immersed in the electrolyte **12** are stationary anode members **13** and a stationary cathode member **14**, both fabricated of partly refined copper. The members **13** and **14** are in contact respectively with beds of particles of partly refined copper **15** and a bed of particles of pure copper **16**. The beds **15** and **16** are fed from the two hoppers **17** and the hopper **18** respectively and fluidized by upward passage of electrolyte supplied through the porous base **21** by lines **19** and line **20** respectively. The anode and cathode compartments are separated by diaphragms **22**. Oversize particles of pure copper are continuously withdrawn through line **23** and passed to a settling tank **24** and thence to hopper **30**. Electrolyte passes from the tank **24** to join the main circulatory system which travels from the cell **11** through line **25** at about the upper level of the fluidized bed in the anode compartment (line **25** is shown for convenience connected to only one of the two compartments). Electrolyte withdrawn through line **25** carries with it undersize particles of impure copper, and flows to a copper settling tank **26**. Fine copper is returned from the tank **26** to the anode feed **17** via a granulator **27** which restores it to a standard size. The electrolyte passes through a slime filter **28** and thence through a control point **29** where pH and other desired characteristics are continuously monitored, before being heated to operating temperature in heat exchanger **9** and returned by a pump **10** via lines **19** to the cell **11**.

Referring to FIG. 2, the cell **31** contains acid zinc sulphate electrolyte **32**. Immersed in the electrolyte **32** are a stationary anode member **33** suitably fabricated of lead or lead alloy and a stationary cathode member **34**, suitably of pure zinc or aluminium. The member **34** is contacted with a bed of particles of zinc **35** which is separated from the anode compartment by a diaphragm **36** and fluidized by upward passage of electrolyte supplied through the porous base **37** via line **38**. The bed **35** is continuously replenished from the hopper **39**, and the anode compartment is fed with zinc oxide, produced by roasting zinc ore, from the hopper **40**. The circulatory system for the electrolyte is substantially as described for FIG. 1, including a heat exchanger **46**, pump **47**, a control point **43** and a settling tank **48** for over-sized particles of zinc withdrawn from the cell **31** from whence they pass to a hopper **49** by way of line **50**, but the copper settling tank **26** and slime filter **28** are replaced by a filter **41** for zinc oxide fines, slimes, etc. which are removed via line **42**. The rate of addition of zinc oxide is controlled by monitoring of pH at the control point **43**. Enough electrolyte is returned through the anode chamber via line **44** to maintain a reasonable degree of agitation and thus promote dissolution of zinc oxide without undue loss thereof by flotation through line **45**.

The effect of soluble impurities such as cadmium and iron may be controlled by the known methods of respective addition of zinc powder and manganese dioxide.

If a calcined zinc oxide feed of sufficient purity to give a coherent electrodeposit is not available, there may be used as feed a zinc sulphate liquor produced by treating roasted ore with partly spent electrolyte containing free sulphuric acid and purified by known methods to remove undesirable trace ingredients such as antimony and cobalt. For this purpose, electrolyte may be withdrawn from the circulatory system at a point downstream of the filter and returned to it upstream of the control point.

It will be understood that although the invention is exemplified above with reference to vertical electrolyte flow through the fluidized bed and vertical stationary electrode members, other arrangements may clearly be used. For example, the cathode member may form a horizontal base of a cell, carrying above it the mobile portion, fluidized by electrolyte flowing in horizontally at the base and then vertically upwards past a horizontal stationary anode, or through a porous member carrying above it a fluidized anode. Alternatively, the stationary anode and/or cathode members may themselves be porous and either electrode member may form the base of the cell up through which the electrolyte flows vertically.

I claim:

1. A process for the electrowinning or electrorefining of metals by electrodeposition in which there is employed a cell containing a cathode, an anode and an electrolyte, the cathode consisting of a bed of small conducting particles containing the metal to be deposited and the anode consisting of a bed of conducting particles, the particles of each bed having a mean diameter of from 20μ to 1000μ and the two beds being separated from each other to prevent intermingling of the particles thereof, each bed being in electrical contact with a stationary conducting member, said process comprising flowing an electrolyte into a lower part of the cell and withdrawing the electrolyte from an upper part of the cell, the upward passage of the electrolyte through the cell being at a rate such that the particles of each bed are fluidised, passing an electric current through the cell by means of the conducting members, the nature of the anode, the electrolyte and the current density being such that the particles of the cathode bed progressively increase in size through electrodeposition of pure metal thereon, continuously withdrawing from the cell particles of the cathode bed of increased size to recover said particles, and replacing the withdrawn particles by fresh particles.

2. A process as claimed in claim **1** wherein the particles constituting the cathode consist of pure metal.

3. A process as claimed in claim **1** wherein the anode consists of a bed of conducting particles, fluidized by the upward passage of electrolyte therethrough, and supplied with a current by a stationary conducting member in contact therewith, the member forming a small part of the total anode area.

4. A process as claimed in claim **3** wherein the conducting particles are metal particles.

5. A process as claimed in claim **3**, wherein the anode conducting member is inert.

6. A process as claimed in claim **3**, wherein the anode conducting member consists of the metal to be recovered in impure or partially refined form.

7. A process for the electrowinning or electrorefining of metals by electrodeposition in which there is employed a cell containing a cathode, an anode and an electrolyte, the cethode consisting of a bed of small conducting particles containing the metal to be deposited and the anode consisting of a bed of conducting particles, the particles of each bed having a mean diameter of from 20μ to 1000μ and the two beds being separated from each other to prevent intermingling of the particles thereof, each bed being in electrical contact with a stationary conducting member and the surface area of each member forming a small part of the total surface area of each bed and each member, said process comprising flowing an electrolyte into a lower part of the cell and withdrawing the electrolyte from an upper part of the cell, the upward passage of the electrolyte through the cell being at a rate such that the particles of each bed are fluidised, passing a direct electric current through the cell by means of the conducting members, the nature of the anode, the electrolyte and the current density being such that the particles of the cathode bed progressively increase in size through electrodeposition of pure metal thereon, continuously withdrawing from the cell particles of the cathode bed of increased size to recover said particles, and replacing the withdrawn particles by fresh particles.

8. A process as claimed in claim **7**, wherein the conducting particles of the anode bed are consumed during operation of the process and particles of the anode bed of decreased size pass upwardly through the cell and out of the cell with the electrolyte and are replaced by fresh particles.

9. A process as claimed in claim **6** wherein the anode is separated from the cathode by a porous diaphragm.

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