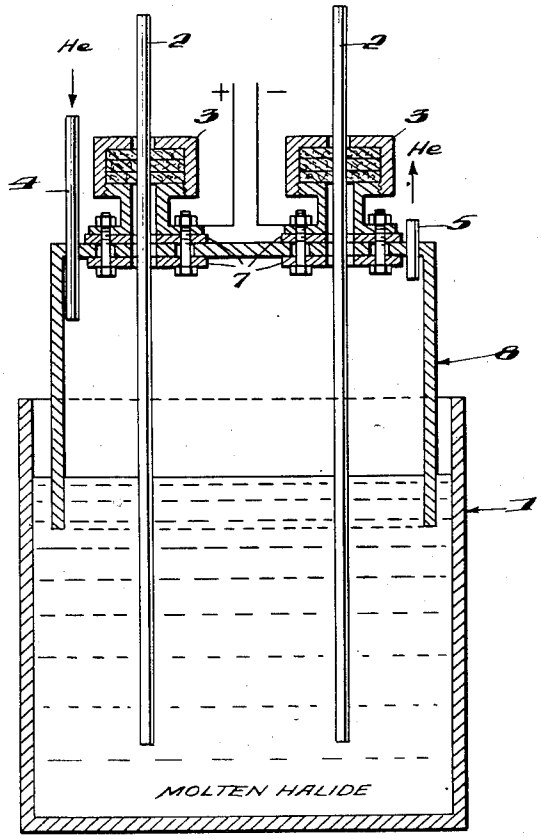
March 26, 1957 B. B. RANEY 2,786,808

PRODUCTION OF TITANIUM

Filed Sept. 22, 1954



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United States Patent Office 2,786,808 Patented Mar. 26, 1957

2,786,808

PRODUCTION OF TITANIUM

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Application September 22, 1954, Serial No. 457,760

7 Claims. (Cl. 204—10)

This application is a continuation-in-part of my application, now abandoned, Serial No. 230,336, filed June 7, 1951, for "Production of Titanium Powder."

In said application the production of finely divided titanium by passing a periodically reversed direct current between titanium electrodes immersed in a fused alkali or alkaline earth metal chloride bath was disclosed.

I have found that the process of this invention is applicable to other metals and alloys.

The use of two similar electrodes with periodic reversals has many advantages over the use of one soluble and one insoluble electrode without reversals: there is no problem of contamination of the deposited metal by the cathode, and no problem of removal of the deposited metal from the cathode.

The process of the present invention is especially valuable in the production of powders from alloys. In this connection the production of alloy powder by the process of my earlier invention may, in some instances, yield a composition differing from that of the anode because of a difference in the diffusion rates of the metal halides formed at the anode. In the process of the present invention the alloy powder formed is of the same composition as that of the metallic portion of the alloy electrodes. This is the result of the formation and reduction processes being separated by only a short time interval during which differential diffusion of the metal halides is insignificant.

My process is also of particular utility in preparing comminuted material from alloys or metals which become passive when made an anode in an electrolytic cell containing fused alkali or alkaline earth halides. This passivity is observed, for example, in tungsten metal and in certain alloys of nickel-chromium and iron-nickel-aluminum cobalt. The mechanism of passivation in the case of these alloys has not been established beyond a doubt; however, it apears highly probable that the passivity results from a slow rate of diffusion of one or more of the halides formed at the anode so that a high resistance film is formed on the anode. Alloys which have this passivation phenomenon cannot be effectively comminuted by an electrolytic process using the procedure of my earlier invention; in the cases of such alloys periodic reversal of the direct current is necessary.

The frequency of reversal of the current in my present invention varies widely, in accordance with the result which it is desired to accomplish. In general, the higher the frequency the better the results. Frequencies of a few reversals per second may be used; however, in general I contemplate using reversal frequencies within the range of from about one per second to about one per five minutes. Alternating currents with reversals of many cycles per second are not satisfactory.

There are several factors which affect the particle size of the metal powder produced. Fine particle size results from the precipitation of metal from a dilute solution of the metal halide by a solution of alkali or alkaline earth metal formed in the cathodic portion of the cycle.

The higher the frequency of current reversal the less chance of dilution of the halide formed in the anodic portion of the cycle and the larger the particle size.

Important electrorefining can be effected by the use of my present invention. Impurities, including oxygen and nitrogen in the transition elements like titanium and zirconium and metallic solutes more noble than the metal being refined, which remain in the residual anode and diffuse therein, can be recovered in the anode skeleton remaining after the electrolysis procedure has been effected. To prevent the solution of the more noble metals the potential of the anode against the solution must be made as low as possible. This is accomplished by adjusting the current density so that during the anodic portion of the cycle the potential of the anode measured against an unpolarized electrode of the same material is not more than 0.1 volt anodic. Under these conditions coarse powders of pure metal form at the electrodes and fall to the bottom of the cell from which they can be removed. The impurities, as noted, can be recovered in the anode skeletons.

The temperature and the composition of the electrolyte are matters of some importance. In general, the higher the temperature the coarser the powder. The electrolyte can be any fused chloride or bromide of alkali and alkaline earth metals. For metals or alloys which are readily oxidized the electrolyte must be free from oxygen and the cell must be protected from the air. I have found that sodium chloride gives larger particles and better refining than other halides of the group. Sodium chloride also has the advantage of being soluble in water without hydrolysis so that it can be removed from the metal product without contamination of the latter.

My invention is applicable to the production of alloy powders from a wide variety of metals and alloys. It is, of course, essential that the metals or alloys be solid at the temperature of the fused salt used and that the chlorides or bromides formed be reducible by alkali and/or alkaline earth metals.

For electrorefining purposes my present invention is particularly applicable to titanium and zirconium containing oxygen.

Having described my invention, I will now illustrate it by examples.

Example I

In this example, I used two titanium electrodes and reversed the direction of current flow from time to time so that both electrodes were consumed and reduced to powder. In this way I prevented any possible contamination of the titanium with the metal of the pot. In this example I used a sillimanite crucible with an inverted nickel bell dipping into a fused mixture of 40 mol. percent of commercial lithium chloride, balance potassium chloride. The construction of the apparatus for this example is illustrated in the single figure of the appended drawing which is a diagrammatic representation of one form of apparatus operable for carrying out the herein process. In the drawing, **1** is a sillimanite pot, **8** is the nickel bell, electrodes **2** and **2** are massive titanium bars, **3** and **3** are packing glands, **4** and **5** are a helium inlet and a helium outlet, respectively, and **7** and **7** are insulating washers. Electrical connections were made to the titanium rods through the packing glands. The temperature of the bath was maintained at about 400° C.

Electrolysis began with 2.7 volts, and the current density was approximately 1 ampere per square inch. The current direction was reversed every five minutes. The titanium bars were evenly attacked and the titanium powder produced was approximately 1 gram per ampere hour. It will be seen from calculation that this corresponds to the solution and deposition of the titanium in

bivalent form. Electrolysis could be continued without loss of efficiency until the suspended titanium powder amounted to 8% of the weight of the electrolyte.

Example II

I proceeded as in Example I except that I used massive titanium containing a minor but significant amount of oxygen as the electrodes. The electrolyte in this example consisted essentially of oxygen-free sodium chloride. The temperature was maintained at approximately 850° C., and the current density at 1000 amperes per square foot. The cell contents were protected by an atmosphere of inert gas. The reversals were at a frequency of one per second. The voltage was .3 volt, approximately .2 of which corresponded to the IR drop in the electrolyte. Electrolysis was continued until residual metal on each electrode was 20% of the original. The titanium sank to the bottom of the cell in the form of coarse particles of titanium of high purity. These particles when fused in an inert atmosphere had a Brinell hardness of 80.

Example III

I proceeded as in Example II except that I used massive zirconium containing oxygen. The product was pure coarse particles of zirconium.

Example IV

In this example I used electrodes of "Alnico," an alloy of iron, aluminum, nickel and cobalt. The electrolyte was a mixture of sodium chloride and potassium chloride, the temperature was about 800° C.; the current density 600 amperes per square foot; reversals, every five seconds; voltage 60 volts. The powdered alloy product was recovered from the bottom of the cell. The magnetic properties of this powder showed that it was a uniform alloy of the same composition and properties as those of the massive material from which the electrodes had been formed.

Example V

In this experiment Example IV was repeated except that the electrodes were formed of "Nichrome V," and the voltage was 4.5. The metal powder product was a uniform alloy of the same composition and properties as those of the massive material.

Example VI

Iron electrodes are immersed in a molten bath of lithium chloride and potassium chloride at 400° C. Reversals occur every five minutes. Iron powder remains in suspension, and the particles are mostly submicron in size.

Molybdenum powder has been produced by the carrying out of this process, which latter is operable also for preparing powders of aluminum, copper, uranium, and a wide variety of other metals more noble than the alkalinous metal employed in the fused salt bath. As was mentioned above, the process has unique applicability to the production of comminuted alloys of the "Nichrome" and "Alnico" categories, and of the category of metals and alloys prone to passivation, but by no means is limited to those categories of metals and alloys.

The particular apparatus used in carrying out the process of the present invention is not critical.

By the expression "alkalinous metal" as used herein and in the appended claims is meant a metal of the group consisting of alkali metals and alkaline earth metals.

I claim:

1. Process of producing comminuted metallic material which comprises the steps of passing a periodically reversed unidirectional direct current between two similar electrodes each being formed of a metallic material selected from the group consisting of titanium, zirconium, tungsten, nickel-chromium alloys and "Alnico," said electrodes being immersed in a molten electrolyte consisting essentially of at least one halide salt of the group consisting of chlorides and bromides of alkalinous metals, said molten bath being maintained at a temperature at which said alkalinous metal salt is molten but below the melting point of the metallic electrodes, the reversal frequencies being within the range of from about one per second to about one per five minutes, whereby to obtain said metallic material, in comminuted form, dispersed in the molten electrolyte.

2. Process as defined in claim 1, in which the current density is maintained at a value greater than 1 ampere per square inch.

3. Process as defined in claim 1, in which the anode potential is maintained at a value not substantially exceeding 0.1 volt anodic.

4. A process for producing a purified comminuted metal from impure massive metal selected from the group consisting of titanium and zirconium, which includes the steps of passing a periodically reversed direct current between two electrodes of the massive metal immersed in a fused bath consisting of at least one halide selected from the group consisting of alkali and alkaline earth metal chlorides and bromides, the reversals in current direction being between one per second and one per five minutes, whereby to form comminuted pure metal dispersed in the fused bath.

5. A process for producing oxygen-free comminuted metal from oxygen-containing metal selected from the group consisting of titanium and zirconium, which includes the steps of passing a periodically reversed direct current between two electrodes of the massive metal immersed in a fused bath consisting of at least one halide selected from the group consisting of alkali and alkaline earth metal chlorides and bromides, the reversals in current direction being between one per second and one per five minutes, whereby to form comminuted pure metal dispersed in the fused bath.

6. Process of producing ductile, substantially pure titanium in comminuted form from a massive material consisting essentially of titanium containing a minor but significant amount of an impurity rendering the same relatively non-ductile, which comprises passing unidirectional direct current between two electrodes formed of said massive material, said electrodes being immersed in an oxygen-free molten electrolyte in an electrolytic cell, said electrolyte consisting essentially of an alkalinous metal chloride maintained at a temperature above the melting point of said chloride but below that of said electrodes, continuously reversing the current direction at a frequency of from one reversal per second to one reversal per five minutes during the electrolysis, maintaining a current density such that during the anodic portion of the cycle the potential of the anode measured against an unpolarized electrode of the same material is not substantially more than 0.1 volt anodic, terminating the passage of periodically reversed current before the electrodes have ceased to be self-supporting but after a substantial amount of particulate titanium of high purity has been formed and has sunk to the bottom of the cell, and thereafter recovering the so-formed particulate titanium from the cell contents.

7. Process of producing ductile, substantially oxygen-free titanium in comminuted form from a massive material consisting essentially of titanium containing a minor but significant amount of oxygen, which comprises passing a unidirectional current between two electrodes formed of said massive material, said electrodes being immersed in an oxygen-free molten electrolyte consisting essentially of sodium chloride maintained at a temperature of approximately 850° C. in an electrolytic cell, continuously reversing the current direction at a frequency of approximately one reversal per second during the electrolysis, maintaining a current density, of approximately 1000 amperes per square foot, such that

during the anodic portion of the cycle the potential of the anode measured against an unpolarized electrode of the same material is not substantially more than 0.1 volt anodic, continuing the passage of periodically reversed current between said electrodes until a substantial amount of each electrode has been consumed and a substantial amount of particulate titanium of high purity has been formed and has sunk to the bottom of the cell, and thereafter recovering the so-formed particulate titanium.

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