In a method for producing metal powder, the first part of an acid-containing starting solution is fed on the anode side of an electrolytic cell as anolyte, to contact the anode and supply material containing yield metal, and a second part of the acid-containing starting solution, which also contains intermediary metal, is fed on the cathode side of the electrolytic cell, to contact the cathode as catholyte. Yield metal is oxidized and dissolved in the anolyte by leading electric current in the anode. The yield metal contained in the second part of the starting solution is reduced on the cathode side. Anolyte solution and catholyte solution are fed to a precipitating chamber for mixing the dissolved, oxidized yield metal and the second part of the starting solution containing reduced intermediary metal.
Start process

S1: Produce starting solution and feed it to the anode and cathode side as electrolyte.

S2: Reduction of intermediary metal on the cathode side, and dissolution and oxidation of yield metal on the anode side.

S3: Bringing anolyte solution and catholyte solution into a precipitation chamber, mixing, and formation of yield metal powder.

S4: Separation of precipitated yield metal powder from circulating solution.

S5: Cleaning the circulating solution and recirculating it back to electrolytic cell.

S6: Finishing treatment of yield metal powder.

Yes

More powder?

No

End process

Fig. 1
Fig. 2

Fig. 3

Cathode side
V^{2+} \rightarrow V^{3+}

Anode side
Cu^0 \rightarrow Cu^{2+}

V^{2+} \rightarrow V^{3+}

V^{3+} \& Cu^{2+} \rightarrow Cu^{2+}

Precipitation chamber
2V^{3+} + Cu^{2+} \rightarrow 2V^{2+} + Cu^0

Cleaning

Circulating solution

Separation

Solid Cu^0

Finishing treatment
METHOD AND ARRANGEMENT FOR PRODUCING METAL POWDER

FIELD OF THE INVENTION

[0001] The invention relates to the production of finely divided metal powder. In particular, the invention relates to a dissolution-precipitation method and arrangement for producing metal powder.

BACKGROUND OF INVENTION

[0002] Generally, the end product in many metal manufacturing processes is a plate-like object in cathode form. This kind of end product is obtained for example by means of pyrometallurgical production routes utilizing electrolysis. In these methods, a metal anode that is pyrometallurgically made of a concentrate is electrolytically refined to cathode copper, which can for example be cast into products with various different forms. These types of methods can be used for producing copper, nickel or cobalt products, among others.

[0003] However, in the production of metals, in many cases it would be advantageous for instance with respect to further processing, if the metal received as the end product of the manufacturing process would be obtained in some other form than as a uniform solid object, such as a cathode plate. Particularly methods where the end product is obtained as pure metal powder would be extremely useful.

[0004] In the patent application JP2002327289, there is introduced a method for producing copper powder in electrolysis. In the method, an aqueous solution of sulfuric acid, containing titanium cathodes, is conducted to an anode chamber, so that the titanium cathodes reduce the copper dissolved in the anode chamber, thus precipitating it in the anode chamber into finely divided copper powder. The problem with this method is that the catholyte solution is conducted directly to the anode chamber where it is not possible to effectively control the mixture ratios of the catholyte solution and the anolyte solution. Moreover, in the method copper is precipitated directly into the anode chamber, which makes it more difficult to remove the precipitated copper from the electrolytic arrangement. These problems constitute a risk for the creation of copper agglomerates, which makes it more difficult to control the particle size of copper powder.

[0005] The patent publication US2005/0023151 introduces a method where copper powder is made by electrolytically precipitating copper from copper sulfate on a cathode. The method makes use of a ferrous/ferric anode reaction, by which the energy consumption of the method is reduced. Said publication also describes a through-flow arrangement where the precipitated copper powder is recovered from the electrodes by means of an electrolyte flowing through the electrodes. A drawback with the method and arrangement illustrated in the publication US2005/0023151 is, among others, an unreliable recovery of copper from the cathodes, owing for example to the precipitation of copper in various different locations in the chamber containing electrodes, and to the attachment of copper on the cathode. Owing to the above mentioned drawbacks, among others, it is difficult to control the grain size of copper powder and of the morphology of copper particles, as well to achieve a homogeneous quality with separate electrodes. In addition, the precipitation of copper directly onto the cathode also depends on the cathode material and on the surface morphology, which in part increases the unreliability of the method.

[0006] The patent application WO2008/017731 introduces a method for manufacturing metal powder. In this method, valuable metal powder is precipitated by reducing the valuable metal dissolved in the method by means of another metal. In said method, also the dissolution of precious metal takes place in a reaction with said other metal, which controls the process kinetics as well as the efficiency thereof, and makes the method and the arrangement used therein fairly complicated.

OBJECT OF INVENTION

[0007] The object of the invention is to eliminate above mentioned drawbacks of the prior art and to set forth a new method and arrangement for manufacturing metal powder in a solution-precipitation method making use of electrolysis.

SUMMARY OF INVENTION

[0008] The method according to the invention is characterized by what is set forth in the independent claim 1.

[0009] The arrangement according to the invention is characterized by what is set forth in the independent claim 20.

[0010] In the method according to the invention for manufacturing metal powder, dissolved yield metal is mixed with a solution containing at least one intermediary metal for precipitating the dissolved yield metal into a yield metal powder.

In the method, a first part of an acid-containing starting solution is brought to the anode side of the electrolytic cell as an anolyte, to be in contact with the anode and the supply material containing yield metal, and a second part of the acid-containing starting solution, which also contains intermediary metal in addition to acid, is brought to the cathode side of the electrolytic cell, as a catholyte to be in contact with the cathode; the yield metal is oxidized and dissolved in the anolyte by conducting an electric current to the anode, the intermediary metal contained in the second part of the starting solution is reduced on the cathode side; and anolyte solution and catholyte solution are brought into a precipitation chamber for mixing the oxidized yield metal dissolved in the first part of the starting solution and the second part of the starting solution containing reduced intermediary metal.

[0011] The arrangement according to the invention is an arrangement for producing metal powder by precipitating yield metal powder by mixing dissolved yield metal powder with a solution containing at least one intermediary metal. The arrangement according to the invention comprises an electrolytic cell for dissolving the yield metal located on the anode side of the electrolytic cell and for oxidizing it in the anolyte, and for reducing, on the cathode side, the dissolved intermediary metal located on the cathode side of the electrolytic cell; a precipitation chamber arranged essentially separately from the electrolytic cell; as well as means for feeding anolyte solution and cathode solution respectively from the anode side and the cathode side of the electrolytic cell to the precipitation chamber for mixing the oxidized yield metal that is dissolved in the anolyte, and the cathode solution containing reduced intermediary metal, outside the electrolytic cell.

[0012] Among the advantages of the invention, let us point out for example good controllability of the particle size of the precipitating yield metal powder, which is made possible particularly by the feeding of the anolyte solution and cathode
solution, to be mixed together, in a separate precipitation chamber, in which case the mixing ratio of said solutions can be controlled easily and accurately, as well as optimized according to the process conditions. Moreover, when the precipitation step takes place in a separate precipitation chamber, away from the vicinity of the electrodes, the effect of the electrodes in the precipitation process and in collecting the precipitate can be minimized, so that the reliability of the process is improved. Also the recovery of the yield metal precipitate becomes easier and more reliable. With a correct mixing ratio and an effective precipitate recovery, the creation of yield metal agglomerates can be prevented in the precipitation step, and consequently the homogeneity of the yield metal particles contained in the powder is enabled with respect to their size. A correct mixing ratio also facilitates a process with a better efficiency, which can be utilized for reducing the amount of energy needed in the process for producing a certain quantity of yield metal mass.

[0013] Unless otherwise stated, in the present document the expressions “anode side” and “cathode side” refer to those parts of the electrolytic cell that contain anolyte or catholyte in the vicinity of the anode or cathode, respectively. The “anode side” or the “cathode side” need not be a uniform part of the electrolytic cell, but the “anode side” or the “cathode side” may consist of several mutually separate elements comprising an anode or a cathode and anolyte or catholyte, respectively.

[0014] Unless otherwise stated, in the present document the expression “diaphragm” refers to any suitable film or thin mechanical obstacle, such as a membrane, an industrial textile or the like.

[0015] Unless otherwise stated, in the present document the expression “oxidation state”, “oxidation level” or a corresponding expression refers to a charge level where an atom appears alone or apparently in a molecule. Thus the expressions “oxidation state”, “oxidation level” or a corresponding expression also refer to the apparent charge of an atom.

[0016] In an embodiment of the invention, the first part of the starting solution contains intermediary metal for boosting the dissolution of yield metal on the anode side. In an embodiment of the invention, the first part of the circulating solution created as a result of mixing the anolyte solution and the catholyte solution is returned to anolyte. In an embodiment of the invention, the first part of the starting solution is composed of the first part of the circulating solution. Further, in an embodiment of the invention, the second part of the circulating solution created as a result of mixing the anolyte solution and the catholyte solution is returned to catholyte. Further, in an embodiment of the invention, the second part of the starting solution is composed of the second part of the circulating solution. Moreover, in an embodiment of the invention, the circulating solution is returned essentially completely back to electrolyte, in which case the circulating solution is essentially composed of the first part of the circulating solution and of the second part of the circulating solution. When an anolyte solution that is formed of the first part of the starting solution and a catholyte solution that is formed of the second part of the starting solution are mixed together, there is created yield metal powder as the yield metal that was oxidized and dissolved in the anolyte is reduced, and the intermediary metal that was reduced in the catholyte is oxidized. The obtained circulating solution is recirculated in an arrangement to be used in the process in one of the embodiments of the invention, so that the circulating solution is partly or completely, after the mixing step and after the yield metal precipitate is separated from the solution, returned back to anolyte and/or catholyte. Now the intermediary metal is again reduced in the catholyte. Thus it is possible to realize an electrolytic regeneration of the intermediary metal in the catholyte, which means that in some embodiments of the invention, it is essentially not necessary to feed in the process new solution containing intermediary metal in solution. We separate the anolyte in some embodiments of the invention contains intermediary metal, said intermediary metal intensifies the dissolution of the yield metal in such process conditions, for example with relatively low acid contents, where dissolution with the combined effect of electric current and acid solution would not be efficient.

[0017] In an embodiment of the invention, the anolyte and the catholyte are mechanically separated by an electrolytic diaphragm. In an embodiment of the invention, the electrolytic cell comprises an electrolytic diaphragm provided in between the anode side and the cathode side of the electrolytic cell for mechanically separating the anode side and the cathode side.

[0018] Further, in an embodiment of the invention, an electrolytic separator solution is conducted in between the two diaphragms separating the anolyte and the catholyte in order to prevent a premature mixing of the anolyte and the catholyte. In an embodiment of the invention, the electrolytic cell comprises two electrolytic diaphragms provided in between the anode side and the cathode side of the electrolytic cell for mechanically separating the anode side and the cathode side by means of an electrolytic separator solution placed in the space between the two diaphragms.

[0019] In order to efficiently separate the precipitation step from the electrolytic cell and to realize this step in a controlled fashion and essentially completely in a separate precipitation chamber, the anolyte and the catholyte can in an embodiment of the invention be separated by means of an electrolytic separator solution. Consequently, the purpose of the diaphragm is to mechanically separate the solutions located on different sides of the diaphragm, i.e. to serve as a mechanical obstacle, while at the same time being electrolytically to that extent that the electrolytic cell is capable of functioning effectively. This diaphragm divides the electrolytic cell to an anode part (or anode side), where the anolyte is located, and to a cathode part (or cathode side), where the catholyte is located. Thus the anolyte and the catholyte cannot be mixed together without disturbing the anode and cathode reactions, and metal powder cannot be formed in the vicinity of those electrodes in the electrolytic cell. For further intensifying the separation of the anode and the cathode, it is possible to use in between the anode side and the cathode side two partition diaphragms, and a separator solution can be fed in between said diaphragms.

[0020] In an embodiment of the invention, the yield metal is copper. In an embodiment of the invention, the yield metal is selected among the following group: nickel, cobalt, zinc, silver, gold, ruthenium, rhodium, palladium, osmium, iridium, platinum, manganese, zirconium, tin, cadmium and indium.
In an embodiment of the invention, the intermediary metal is vanadium. Further, in an embodiment of the invention, the intermediary metal is selected among the following group: titanium, chromium and iron. Further, in an embodiment of the invention, the intermediary metal is selected among the following group: manganese, zirconium, molybdenum, technetium, tungsten, quicksilver, germanium, arsenic, selenium, tin, antimony, tellurium and copper. In the various embodiments of the invention, the yield metals and intermediary metals can be selected among a group that depends on various different process parameters, particularly on the pH value of the electrolyte (i.e. on the oxygen content). On the basis of the description of the invention, a man skilled in the art is capable of finding in the literature for example group IV, suitable intermediary metal for a certain yield metal by means of routine testing. In particular, it has been found out that for example copper powder can be efficiently and reliably produced in an embodiment of the invention, when the selected intermediary metal is vanadium.

In an embodiment of the invention, the supply material containing yield metal is placed in the anode. Further, in an embodiment of the invention, the yield metal located on the anode side of the electrolytic cell is placed in the anode of the electrolytic cell. When the supply material containing yield metal is placed in the anode, the rate per unit time of the electric current passing through the yield metal, and consequently also the mass of the dissolving yield metal per unit of time, can be efficiently controlled. The advantage of this embodiment is a particularly precise control of the dissolving reaction by means of electricity; yield metal is dissolved accurately according to the used quantity of electricity in the course of the given time period according to Faraday’s laws. Moreover, the kinetics in the dissolution step are rapid, as the quantity of yield metal dissolved in the anolyte is directly proportional to the charge that has flown through the anode. Thus also the quantity of yield metal that is dissolved in the anolyte can be efficiently and accurately controlled, which facilitates a more precise control of the process dynamics, and an improvement in reliability.

In an embodiment of the invention, the yield metal is selected so that the selected yield metal is dissolved in the anolyte as a soluble salt of the acid that is contained in the first part of the starting solution.

In an embodiment of the invention, the electrolytes are placed in an oxygen-free environment, in order to prevent the oxidation of the yield metal and/or intermediary metal that is contained in the electrolytes. This makes it easier to control the acid content of the electrolytes, which means that the balance of chemical reactions taking place in the different solutions of the process and containing for example yield metal and/or intermediary metal can be adjusted more accurately, which in turn improves the reliability and efficiency of the process, among others.

In an embodiment of the invention, the starting solution contains sulfuric acid. Further, in an embodiment of the invention the sulfuric acid content in the starting solution is at least 50 g/l and preferably within the range 50 g/l-1,500 g/l. In an embodiment of the invention, the starting solution contains hydrochloric acid or nitric acid. Further, in an embodiment of the invention the hydrochloric acid content in the starting solution is within the range 15 g/l-500 g/l. Yet in an embodiment of the invention the starting solution contains, in addition to hydrochloric acid, also alkaline chloride, the content of which in the starting solution is within the range 15 g/l-500 g/l. The suitability of an acid in the starting solution depends, among others, on the supply material, the yield metal and the intermediary metal in question. In some embodiments of the invention, the solutions may also contain more than one acid. On the basis of the description of the invention, a man skilled in the art is capable, by routine testing, of finding a suitable acid for a certain supply material, yield metal and intermediary metal, and a suitable content for said acid. In particular, it has been found out that in some embodiments of the invention, a sulfuric acid content of the starting solution that is at least 50 g/l provides for an efficient oxidation of a copper anode and its dissolution in the anode, when the intermediary metal is vanadium. A suitable acid, and content for said acid, must be chosen so that the yield metal is dissolved from the supply material to the anolyte, instead of the oxidation of the intermediary metal. Therefore the anolyte pH (i.e. oxygen content) must be suitable. When the employed yield metal is copper, and the intermediary metal is vanadium, the oxygen content must be as high as possible.

In an embodiment of the invention, the electrolytic cell comprises at least one bag defined by a diaphragm in order to restrict the anolyte and/or catholyte inside the bag. Further, in an embodiment of the invention the electrolytic cell comprises means for conducting the separator solution from a space left in between two diaphragms to the anode side and/or the cathode side.

The above described embodiments of the invention can be freely combined with each other. Several different embodiments can be combined in order to create a new embodiment. A method or arrangement that the invention relates to can include one or several of the above described embodiments of the invention.

DETAILED DESCRIPTION OF INVENTION

In the specification below, the invention is described with reference to the appended drawings, where

FIG. 1 is a flowchart illustrating an embodiment of a method according to the invention.

FIG. 2 is a schematic illustration of an embodiment of an arrangement according to the invention.

FIG. 3 is a schematic block diagram illustrating an embodiment of a method according to the invention.

FIG. 4 is a schematic illustration of an embodiment of the electrolytic cell in an arrangement according to the invention.

FIG. 5 shows scanning electron microscope images (SEM images) of copper powder produced by an embodiment of the invention.

For the sake of simplicity, reference numbers referring to various elements of the invention remain the same in connection with corresponding repeated elements.

In the preparation step S1 of an embodiment of the method according to FIG. 1, there is produced and fed into the electrolytic cell, both to the anode side and to the cathode side, acid-bearing starting solution, electrolyte solution, which contains intermediary metal in its high potential value (i.e. in a higher oxidation state). In the method it is essential that at least the second part of the starting solution, which is fed to the cathode side, contains said intermediary metal in its high potential value, because in step S2, in the catholyte there is carried out the reduction of the intermediary metal to its low potential value (i.e. to a lower oxidation state), i.e. the regeneration of the intermediary metal. Also the first part of the starting solution, i.e. the part that is fed as the anolyte, may
contain intermediary metal in its high potential value. In some
embodiments of the invention, the starting solution may con-
tain two or even several different intermediary metals. In
some embodiments of the invention, the first and second part
of the starting solution are identical in composition. By this
procedure, the possibility that the composition of the electro-
lytes would be changed after starting the process is mini-
mized, which means that the operating point of the process is
stabilized more rapidly, and the controllability of the process is
improved.

[0036] The type of intermediary metal suited in the method
essentially depends on the selected yield metal, which should
be dissolved in the anolyte in step S2, and which is later
precipitated into powder in the mixing step S3. The interme-
diary metal and the selected yield metal together define the
other features of the starting solution suited in the method,
particularly the acid contained in the solution, and content of
said acid in the solution. For example, the pH value of the
solution must be such that in the prevailing process condi-
tions, on the anode side there is more advantageously carried
out the oxidation of yield metal and its dissolution in the
anolyte than the oxidation of the intermediary metal in the
anolyte. This kind of process conditions, i.e. functional win-
dows, can be found for many different pairs of yield metal
and intermediary metal. In the light of the description of the
present invention as well as in the light of the Pourbaix dia-
grams of various different intermediary metals and yield met-
als, the finding of these functional windows represents rou-
tine testing for a man skilled in the art.

[0037] The starting solution can be produced in many dif-
ferent ways, which depend, among others, on the suitable
intermediary metal. One way is for example to dissolve, in an
aqueous solution of a suitable acid, oxide containing the
desired intermediary metal. When necessary, the acid content
of the starting solution and the oxidation number of the dis-
solved intermediary metal can thereafter be adjusted to be
suitable with respect to the starting solution. The adjusting
of the oxidation number of the intermediary metal can be car-
ried out for example electrolytically.

[0038] When the starting solution is formed in step S1, it is
fed as electrolyte in an electrolytic cell, where supply material
containing yield metal is located on the anode side. In a
method according to FIG. 1, after step S1, in step S2 yield me-
tal is dissolved on the anode side of the electrolytic cell from
the supply material to the anolyte, as the yield metal is at the same
time oxidized, and on the cathode side the intermediary metal
of the starting solution is reduced from a high potential value
to a low potential value. Because of production consider-
ations, among others, it is advantageous that the intermediary
metal content and the content of the dissolved yield metal in
the solutions is as high as possible. Thus a certain solution
volume gives more precipitated yield metal powder in the
mixing step S3, than in a situation where the contents of the
intermediary metal and/or dissolved yield metal in the solu-
tions are low.

[0039] The method according to FIG. 1 can be realized by
means of an arrangement illustrated schematically in FIG. 2,
where the employed supply material is present as an anode 2,
which provides for rapid kinetics in the dissolution of yield
metal, while the dissolution of the supply material is directly
proportional to the charge flowing through the anode 2. Now
the dissolution reactions can be controlled particularly accu-
rately by using electricity; in a given period of time, the mass
quantity of yield metal dissolved and oxidized on the anode is
accurately proportional to the employed quantity of electric-
ity, according to Faraday’s laws. Respectively, an equimolar
quantity of the intermediary metal is regenerated (reduced)
on the cathode. The arrangement of FIG. 2 also comprises a
cathode 4, an anode side 6 of the electrolytic cell, a cathode
side 8, anolyte filtering equipment 10, a precipitation cham-
ber 12, separator equipment 16, and cleaning equipment 18
for the circulating solution. The anolyte 1 and the catholyte 3
are mechanically separated by means of an electroconductive
separator solution 5 placed in the intermediate space 11 and
by means of two electroconductive diaphragms 7 that define
the intermediate space. The purpose is to ensure that the yield
metal cations created on the anode side and the intermediary
metal that is reduced on the cathode side do not get into mutual
contact in the electrolytic cell. Thus yield metal powder cannot be precipitated directly on
the anode or cathode side of the electrolytic cell, which
would, in case it happened, weaken the controllability of the
process for example as regards the particle size of the yield
metal powder as well as the process efficiency, and in addi-
tion, the recovery of the yield metal powder would become
more difficult. In order to improve the separation of the
anolyte 1 and the catholyte 3, the separator solution 5 pro-
vided in the intermediate space 11 can also be maintained at
a higher hydrostatic pressure than the anolyte 1 and the
catholyte 3.

[0040] After step S2, in step S3, anolyte solution is con-
ducted from the anode side of the electrolytic cell and
catholyte solution is conducted from the cathode side thereof,
for example by means of suitable pipes or in some other way,
to the precipitation chamber 12, in a suitable ratio away from
the vicinity of the electrodes 2, 4. Because anolyte solution
and catholyte solution are conducted to a separate precipita-
tion chamber 12, the mixing ratio of the solutions can be
controlled easily and accurately, and it can be optimized
according to the process conditions. With a correct mixing
ratio and an effective precipitate recovery, the creation of
yield metal agglomerates can be prevented in the precipita-
tion step, and consequently the homogeneity, with respect to
their size, of the yield metal particles contained in the yield
metal powder 14 is ensured. A correct mixing ratio also facili-
tates a process with a better efficiency, which results in reduc-
ing the amount of energy needed in the process for producing
a certain quantity of yield metal mass.

[0041] In the precipitation chamber 12, there is mixed, or
there can be continuously mixed the anolyte solution and the
catholyte solution conducted in the chamber 12. Prior to
conducting the anolyte solution into the precipitation cham-
ber 12, it can in some embodiments of the invention be also
purified of metallic impurities and/or other possible impuri-
ties disturbing the yield metal precipitation process in an
anolyte filtering equipment 10 that is suited for this purpose.
As a result of the mixing process, the oxidized yield metal of
the anolyte solution is reduced and precipitated into solid
yield metal powder 14, at the same time as the intermediary
metal reduced in the catholyte solution is oxidized back to its
high-potential value. From the obtained circulating solution,
there is separated, in step S4, yield metal for example by
centrifuging the circulating solution in separator equipment
16 suited for the purpose.

[0042] When the yield metal powder 14 is recovered, the
created circulating solution is recirculated back to the elec-
trytic cell in step S5, part of it into anolyte 1 and part into
catholyte 3. Before conducting the circulating solution back
to the electrolytic cell, any dissolved yield metal that is possibly left in the circulating solution is removed therefrom, as well as yield metal particles, in cleaning equipment 18 suited for this purpose. The cleaning operation can be carried out for example electrolytically by reduction and filtering. A thorough removal of yield metal, both dissolved and precipitated, from the circulating solution prior to recirculating the circulating solution back to the electrolytic cell is useful for the reliability of the process, for improving process efficiency and the controllability of the particle size of the yield metal powder.

In the above described method, the composition of the circulating solution is essentially identical with the composition of the starting solution, because in precipitation, the intermediary metal is oxidized back into its starting solution value, and the yield metal dissolved in the anolyte 1 on the anode side is precipitated and separated from the solution. Thus the circulating solution created in the method can be reused as a starting solution. If also the recirculating of the circulating solution back to anolyte and catholyte is carried out with the same ratio that was applied when a corresponding electrolyte was fed from the anode side and the cathode side to the precipitation chamber in step S3, an essentially closed electrolyte circulation can be used in the process, without a need to separately add/remove solution to or from the anode side 6 of the electrolytic cell, or to or from the cathode side 8.

In practice, the method of FIG. 1 is generally realized as a continuous electrolyte circulation, as a result of which in the precipitation chamber 12 there is continuously anolyte and catholyte powder 14 to be separated from the circulating solution and to be recovered, until the recirculation of the electrolyte solution (circulating electrolyte) in the arrangement is stopped, or when the yield metal contained in the supply material (anode 2) is completely dissolved in the electrolytic cell. When there is no more need to produce yield metal powder 14, or when the yield metal of the supply material is finished on the anode side 6 of the electrolytic cell, the recovered yield metal powder 14 is treated in a finishing treatment in step S6, and the process is stopped. In some other preferred embodiments of the invention, the finishing treatment for the recovered yield metal powder 14 can be carried out simultaneously with the other steps of the process, in the course of the process of separating yield metal powder 14 and feeding it to the finishing treatment equipment (not illustrated).

In an example according to FIG. 3, illustrated as a block diagram, the employed intermediary metal is vanadium, which in its high-potential value is $V^3+$ in cations. The employed yield metal is copper, which is located in the supply material serving as the anode 2. The starting solution containing the vanadium intermediary metal in $V^3+$ cations can be produced for instance by dissolving vanadium oxide $V_2O_5$ for instance to an aqueous solution of sulfuric acid. When the starting solution that contains $V^3+$ cations in an aqueous solution, the sulfuric acid content of said solution being for example within the range 50 g/l-1500 g/l, is formed, its first part is fed to the anode side 6 of the electrolytic cell as the anolyte 1, and the second part is fed to the cathode side 8 as the catholyte 3. When electric current flows through the electrolytic cell, the $V^3+$ cations are reduced on the cathode side 8 to $V^{2+}$ cations in the catholyte 3, and copper is dissolved from the anode 2 to the anolyte 1 as oxidized $Cu^{2+}$ cations. Consequently, the anode reaction is $Cu^{2+}$ -> $Cu^{2+}2e^-$, and the cathode reaction is $V^{3+}+2e^->V^{2+}$.

In the dissolution of copper and its oxidation in the anolyte 1, the intermediary metal may in some embodiments of the invention participate in corresponding reactions, thus improving both dissolution and oxidation, in such process conditions, for example with fairly low acid contents, where dissolution and oxidation with the combined effect of a mere electric current and an acid solution would not be efficient. Now the precise mechanism how the intermediary metal participates in the dissolution and oxidation of the yield metal depends on the selected yield metal and intermediary metal. In the above described example, when the yield metal is copper and the intermediary metal is vanadium, vanadium may be oxidized on the anode side 6 into an intermediary oxidation state $V^{3+}$, which is higher than its original potential value, whereby the $V^{3+}$ reacts with copper, thus oxidizing and dissolving copper. Now the “over-oxidized” vanadium $V^{3+}$ is reduced back to its original high-potential value $V^{2+}$. On the anode side 6, a corresponding “overoxidation” to an intermediate oxidation state is also possible with other intermediary metals than vanadium.

Thereafter anolyte solution and catholyte solution are conducted and mixed in a suitable ratio, for example in the ratio 1:3, in the precipitation chamber 12, where copper is precipitated through the reaction $2V^{2+}+Cu^{2+} -> 2V^{3+}+Cu^{0}$. On the basis of this precipitation reaction, anolyte and catholyte are in theory needed in the mixing ratio 1:2, in order to make all $V^{3+}$ and $Cu^{2+}$ cations present in the solutions participate in the precipitation of copper. An optimal mixing ratio depends on the reaction state of the anode reactions and on the current efficiency, as well as on the reaction state and current efficiency of the cathode reactions.

As regards the efficiency and reliability of the process, it is useful to ensure that any remarkable amounts of $V^{2+}$ and/or $Cu^{2+}$ cations are not left in the circulating solution. In some embodiments of the invention, it is for example advantageous to try and make sure that all $Cu^{2+}$ cations are consumed in the precipitation reaction, in which case the real mixing ratio of anolyte and catholyte can be 1:N, where N=2. However, the value of the parameter N also depends on how the circulating solution is cleaned before feeding it back to the electrolytic cell. On the basis of the description of the present invention, the finding of a suitable mixing ratio is obvious routine testing for a man skilled in the art.

When copper is precipitated into powder 14 and separated from the rest of the solution by means of the separator equipment 16, the remaining circulating solution is cleaned in the cleaning equipment 18 of any copper that is possibly left in the solution in the separation process, both of solid copper and dissolved, unpurified $Cu^{2+}$ cations. The cleaning can be carried out for example electrolytically by precipitating and filtering. After said chemical and mechanical cleaning, the remaining circulating solution is essentially the same in composition as the starting solution, containing as a result from the precipitation reaction vanadium cations $V^{2+}$ and sulfuric acid in aqueous solution. This circulating solution is again divided in a suitable ratio into anolyte 1 on the anode side 6 and into catholyte 3 on the cathode side 8. After the above described regeneration, the same circulation electrolyte can again be conducted through the arrangement and the method for precipitating more/new copper powder 14 to the precipitation chamber 12.

The solid yield metal powder 14 separated from the solution is finished (FIG. 1, step S6) in a finish treatment arrangement. The separation and finish treatment processes
can include many different steps, depending on the desired properties of the end product. In some embodiments of the invention, the yield metal powder 14 separated from the circulation electrolyte is washed in water for minimizing impurities carried along from the solution, whereafter the yield metal powder 14 is dried and coated with a passivation layer for preventing an oxidation of the powder, among others. In order to minimize the redissolution of the precipitated yield metal powder 14 back into the circulating solution, it is useful to perform the separation of the yield metal powder 14 from the circulating electrolyte by the separator equipment 16, and it is advisable to perform the washing as quickly as possible after the precipitation reaction.

[0051] In some embodiments of the invention, the yield metal powder 14 is subjected to various separate washing operations. In between the washing operations, the yield metal powder 14 is separated from the washing liquid. In an embodiment of the invention, the yield metal powder 14 that is obtained from the separator equipment 16, which is separated from the circulating electrolyte by centrifuging but is still wet, is mixed in water in the mass mixing ratio 1:20 (one part of wet yield metal powder 14 and 20 parts of water) three times. In between the mixing operations, the yield metal powder 14 is separated from the washing liquid.

[0052] The exact structure and operation of the washing equipment can vary even to a great extent, and for a man skilled in the art, a production of such equipment is obvious in the light of the description of the present invention. In a preferred embodiment of the invention, the washing equipment for realizing several successive washing operations can be for example a conveyor-belt type arrangement, where the wet yield metal powder 14 is poured on a conveyor belt, which conveys the yield metal powder 14 to the washing liquid, from which the yield metal powder is poured on the next conveyor belt, etc. Now the setting of the yield metal powder 14 takes place when it is separated from the washing liquid, i.e. when the washing liquid containing yield metal powder is poured on the conveyor belt.

[0053] In addition to the above described example, or instead of the procedure described therein, the separated yield metal powder can naturally also be washed by many known methods, for example by means of a spout.

[0054] Various different electrolytic cell structures can be designed for dissolving and oxidizing yield metal on the anode side of an electrolytic cell, and for reducing intermediary metal on the cathode side of an electrolytic cell. The electrolytic cell structure illustrated schematically in FIG. 4 can be used in the arrangement for producing yield metal powder 14 in a reliable and efficient way, with a good efficiency.

[0055] In the electrolytic cell of FIG. 4, both the anode side 6 and the cathode side 8 comprise several sections, i.e. diaphragm bags, defined by a diaphragm 7. Each diaphragm bag respectively includes a diaphragm 2 or a cathode and anolyte 1 or catholyte 3. Naturally the anodes 2 and the cathodes 4 are connected to a power source (not illustrated). In between each diaphragm 7, there is a predefined electrolytic cathode solution 5, which in case the embodiment of the invention contains intermediary metal in a suitable high-potential value, i.e. in an oxidized state, in the case of the above described example, the separator solution 5 may contain for example V₃O₅ ions.

[0056] In addition, the electrolytic cell of FIG. 4 comprises a feed pipe 9 for feeding separator solution to the intermediate space 11 left between the diaphragm bags, an overflow channel 13 for the separator solution 4, drain channels 15 for the anolyte solution and the catholyte solution, as well as a protective film 17. The electrolytic cell of FIG. 4 can be connected to another arrangement, for example to a precipitation chamber 12 (not illustrated in FIG. 4), by interconnection of the drain channels 15 and the feed pipe 9.

[0057] In an embodiment of the invention, the separator solution 5 serves as the starting solution, in which case the composition of the separator solution 5 is identical to that of the starting solution. Now the starting solution can be fed to the intermediate space 11 of the electrolytic cell illustrated in FIG. 4 through the apertures provided in the feed pipe 9. From the intermediate space 11, the separator solution 5 flows to the diaphragm bags as anolyte 1 and catholyte 3 through perforations provided in the diaphragms 7. In addition or instead, the diaphragm can be semi-permeable, so that the separator solution 5 (starting solution) has access to flow in a controlled fashion through the diaphragm 7 as anolyte 1 and/or catholyte 3. Anode reactions and cathode reactions take place in the diaphragm bags in the way described above. The obtained catholyte solution, containing reduced intermediary metal, as well as the anolyte solution containing dissolved or oxidized yield metal, can be conducted to the precipitation chamber 12 for example through outlets 15. In some embodiments of the invention, the outlets 15 can serve as overflow channels for removing excess electrolyte from the arrangement, in which case anolyte solution and/or catholyte solution can be brought in the precipitation chamber 12 via another route, for example through suction inlets provided for this purpose. The circulating solution created in the precipitation chamber 12 can in turn be recirculated, after possible cleaning steps, for example via a feed pipe 9 back to the intermediate space 11 and further to anolyte 1 and/or catholyte 3.

[0058] By adjusting the permeability of the diaphragms 7 in the cell illustrated in FIG. 4, or the size of the perforations provided in the diaphragms 7, the quantity of the solution flowing through the anode side 6 and/or the cathode side 8 per unit of time can be efficiently controlled. The permeability of the diaphragms 7 can be selected separately for the diaphragms 7 on the anode side 6 and/or for the diaphragms 7 on the cathode side 8. By suitably controlling the quantity of solution per time unit that has access to flow in the diaphragm bags on the anode side 6 and/or on the cathode side 8 through the diaphragms 7, in relation to the quantity of solution per time unit to be fed in the intermediate space 11, the hydrostatic pressure of the separator solution 5 placed in the intermediate space 11 can be adjusted to be higher than the hydrostatic pressure of the electrolytes contained in the diaphragm bags located in the separator solution 5. Thus it is possible to prevent an undesired flowing of the electrolyte through the diaphragm 7 towards the intermediate space 11, away from the diaphragm bag. By suitably arranging the measures of the overflow channel 13, for example by arranging it at a suitable height, it is possible to ensure according to FIG. 4 that the hydrostatic pressure difference between the intermediate space 11 and the anode side 6 and/or the cathode side 8 does not rise too high, but any excess separator solution flows out of the cell through the overflow channel 13. Respectively, also by arranging the measures and locations of the outlets 15, it is possible to affect the formation of said hydrostatic pressure difference. When the diameter of the perforations possibly provided in the diaphragms 7 is large, said hydrostatic pressure difference, together with the permeability of the di-
phragsms 7, essentially defines the quantity of solution that flows through the anode side 6 and the cathode side 8 per unit of time. On the basis of the description of the present invention, the above described design of the measures of the electrolytic cell, and the placing of the perforations, is obvious routine testing for a man skilled in the art.

[0059] As was described above, in some embodiments of the invention it is not necessary to directly feed starting solution and/or circulating solution to the anode side 6 and/or cathode side 8 of the electrolytic cell, for example to the diaphragm bags, but essentially all solution in the arrangement circulates through the intermediate space 11. In case the diaphragms 7 are selected to be such that they are completely impermeable to solution, circulating solution and/or starting solution can be fed to the anode side 6 and/or to the cathode side 8, for example to the diaphragm bags, directly and not through the intermediate space 11. In some other embodiments of the invention, instead of the diaphragms 7, there can be used for example ion-selective membranes that only permeate ions of a certain type.

[0060] In the electrolytic cell according to FIG. 4, the electrolytic cell structure is covered by a protective film 17, by means of which the intermediate space 11 can be pressurized for example with nitrogen gas or with some other inert gas in order to prevent a possible oxidation caused by air or the surrounding environment. Also the diaphragm bags can be closed and pressurized with nitrogen in order to prevent oxidation.

[0061] The cell structure of FIG. 4 enables a reliable separation of the anolyte and the catholyte in the electrolytic cell, which reduces premature oxidation and/or reduction reactions. Consequently, by using the electrolytic cell structure according to FIG. 4, there is achieved a high efficiency in the method. In addition, the risk of a premature precipitation of the yield metal powder in the electrolytic cell is reduced, which improves the reliability of the method and makes the maintenance of the equipment easier.

EXAMPLE

[0062] By applying a method according to the block diagram illustrated in FIG. 3, there was manufactured, in an arrangement representing essentially the type illustrated in FIG. 2, copper powder by employing as the starting solution an aqueous solution of sulfuric acid, said solution containing V$^{5+}$ cations. In this starting solution, the measured sulfuric acid concentration was about 500 g/l, and the measured vanadium concentration was about 16 g/l. The employed supply material was Class A cathode copper plate, which also served as the anode of the electrolytic cell. The employed cathode was a lead plate, measures 275 mm x 130 mm. In test conditions, the solution temperatures were roughly 20-35°C.

[0063] The starting solution was fed to the electrolytic cell, where copper anode was oxidized and dissolved in the anolyte. The measured content of the dissolved copper was roughly 4 g/l. Thereafter anolyte solution was conducted from the anode side, and catholyte solution was conducted from the cathode side to the precipitation chamber, which in this example was a glass bottle. The mixing ratio of the anolyte solution and the catholyte solution was 1:3. As a result of the mixing operation, copper powder was formed in the precipitation chamber, according to the description above. The electron microscope images taken of the obtained copper powder are illustrated in FIG. 5; from these images it can be observed, for example, that the size distribution of the copper particles is fairly homogeneous, large particle agglomerates are not created, and the average size of the particles is below the micrometer range.

[0064] Although some examples and embodiments illustrating the invention are above described as methods for manufacturing copper powder, a man skilled in the art is on the basis of this description of the invention easily capable of manufacturing powders also of other metals than copper when applying the various embodiments of the invention. Likewise, on the basis of this description of the invention, a man skilled in the art is easily capable of using, in the various embodiments of the invention, other intermediaries and/or acids than those enlisted in the above examples. The invention is not restricted to the above described examples only, but it can be realized in many different modifications within the scope of the appended claims.

1. A method for manufacturing metal powder, wherein dissolved yield metal is mixed with a solution containing at least one intermediary metal for precipitating the dissolved yield metal into yield metal powder (14), wherein in the method

   a. a first part of an acid-containing starting solution is brought as an anolyte (1) to the anode side (6) of an electrolytic cell, to be in contact with the anode (2) and the supply material containing yield metal; and a second part of the acid-containing starting solution, which also contains intermediary metal in addition to acid, is brought to the cathode side (8) of the electrolytic cell, as a catholyte (3) to be in contact with the cathode (4);

   b. the yield metal is oxidized and dissolved in the anolyte (1) by conducting electric current in the anode (2);

   c. the intermediary metal contained in the second part of the starting solution is reduced on the cathode side (8); and

   d. anolyte solution and catholyte solution are brought into a precipitation chamber (12) for mixing the oxidized yield metal dissolved in the first part of the starting solution and the second part of the starting solution containing reduced intermediary metal.

2. A method according to claim 1, wherein the first part of the starting solution contains intermediary metal for boosting the dissolution of yield metal on the anode side.

3. A method according to claim 1, wherein the first part of the circulating solution created as a result of mixing the anolyte solution and the catholyte solution is returned back to anolyte (1).

4. A method according to claim 3, wherein the first part of the starting solution is composed of the first part of the circulating solution.

5. A method according to claim 3, wherein the second part of the circulating solution created as a result of mixing the anolyte solution and the catholyte solution is returned back to catholyte (3).

6. A method according to claim 5, wherein the second part of the starting solution is composed of the second part of the circulating solution.

7. A method according to claim 5, wherein the circulating solution is conducted essentially completely back to electrolyte, so that the circulating solution is essentially composed of a first part of the circulating solution and of a second part of the circulating solution.
8. A method according to claim 1, wherein the anolyte (1) and the catholyte (3) are mechanically separated by an electroconductive diaphragm (7).
9. A method according to claim 1, wherein electroconductive separator solution (5) is conducted in between the two diaphragms (7) separating the anolyte (1) and the catholyte (3) in order to prevent a premature mixing of the anolyte (1) and the catholyte (3).
10. A method according to claim 1, wherein the yield metal is copper.
11. A method according to claim 1, wherein the yield metal is selected among the following group: nickel, cobalt, zinc, silver, gold, ruthenium, rhodium, palladium, osmium, iridium, platinum, manganese, zirconium, tin, cadmium and indium.
12. A method according to claim 1, wherein the intermediary metal is vanadium.
13. A method according to claim 1, wherein the intermediary metal is selected among the group titanium, chromium and iron.
14. A method according to claim 1, wherein the intermediary metal is selected among the following group: manganese, zirconium, molybdenum, technetium, tungsten, quicksilver, germanium, arsenic, selenium, tin, antimony, tellurium and copper.
15. A method according to claim 1, wherein the supply material containing yield metal is located in the anode (2).
16. A method according to claim 1, wherein the yield metal is selected so that the chosen yield metal is dissolved in the anolyte (1) as a soluble salt of the acid that is contained in the first part of the starting solution.
17. A method according to claim 1, wherein the starting solution contains sulfuric acid.
18. A method according to claim 1, wherein the content of sulfuric acid in the starting solution is at least 50 g/l and preferably 50 g/l-1500 g/l.
19. A method according to claim 1, wherein the starting solution contains hydrochloric acid or nitric acid.
20. An arrangement for producing metal powder by precipitating yield metal powder (14) by mixing dissolved yield metal with a solution containing at least one intermediary metal, wherein the arrangement comprises an electrolytic cell for dissolving the yield metal located on the anode side of the electrolytic cell and for oxidizing it in the anolyte, and for reducing the dissolved intermediary metal located on the cathode side (8) of the electrolytic cell on the cathode side; a precipitating chamber (12) that is essentially separate from the electrolytic cell; as well as means for feeding anolyte solution and catholyte solution respectively from the anode side (6) of the electrolytic cell and from the cathode side (8) of the electrolytic cell to the precipitating chamber (12) for mixing the yield metal dissolved in the anolyte and the catholyte solution containing reduced intermediary metal, from outside the electrolytic cell.
21. An arrangement according to claim 20, wherein the electrolytic cell comprises an electroconductive diaphragm (7) in between the anode side (6) and the cathode side (8) of the electrolytic cell for mechanically separating the anode side (6) and the cathode side (8).
22. A method according to claim 20, wherein the electrolytic cell comprises two electroconductive diaphragms (7) in between the anode side (6) and cathode side (8) of the electrolytic cell for mechanically separating the anode side (6) and the cathode side (8) by means of an electroconductive separator solution (5) provided in the space left between the two diaphragms (7).
23. A method according to claim 20, wherein the yield metal supplied on the anode side (6) of the electrolytic cell is located in the anode (2) of the electrolytic cell.
24. A method according to claim 20, wherein the electrolytic cell comprises at least one bag, defined by a diaphragm (7), for keeping the anolyte and/or the catholyte inside the bag.
25. A method according to claim 20, wherein the electrolytic cell comprises means for conducting a separator solution (5) from the space left between the two diaphragms (7) to the anode side (6) and/or to the cathode side (8).
26. A method according to claim 20, wherein the electrolytes are placed in an oxygen-free environment for preventing the oxidation of the yield metal and/or intermediary metal contained in the electrolytes.

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