June 3, 1952 G. RENMAN 2,598,833

PROCESS FOR ELECTROLYTIC DEPOSITION
OF IRON IN THE FORM OF POWDER
Filed July 5, 1947

FIG. 1

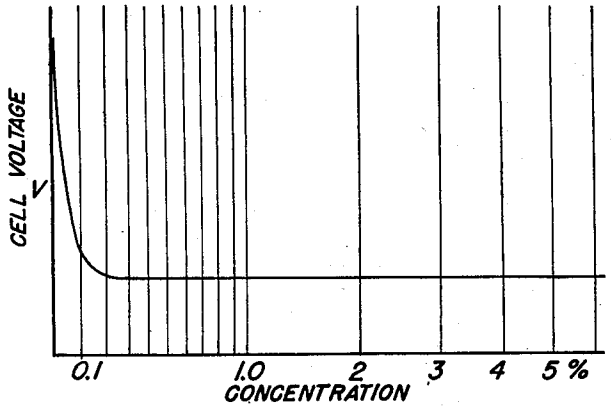
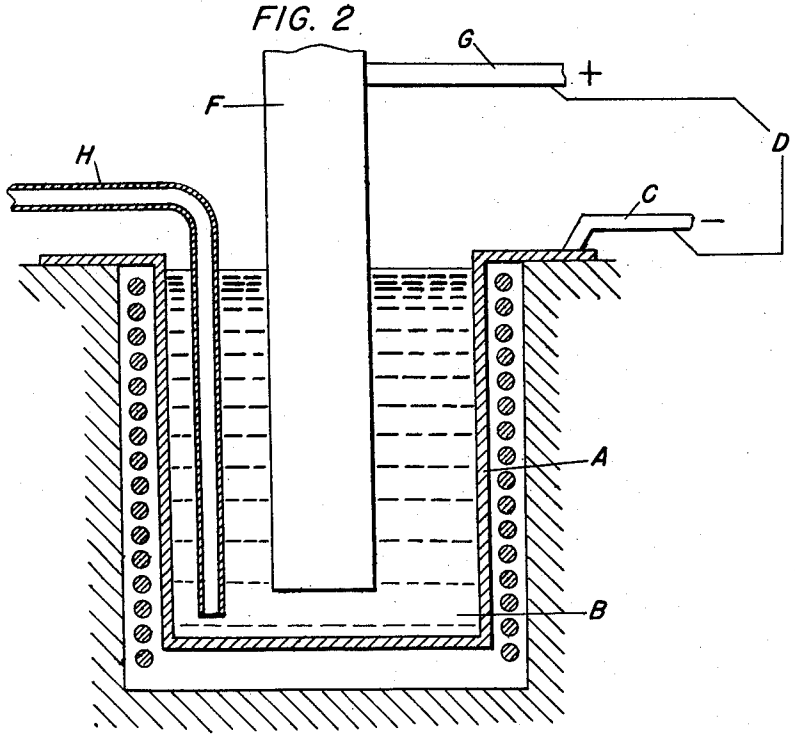


FIG. 2



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PROCESS FOR ELECTROLYTIC DEPOSITION OF IRON IN THE FORM OF POWDER

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3 Claims. (Cl. 204—10)

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This invention relates to electrolytic deposition of metals in the form of powder and particularly to methods for such electrolytic deposition in which an anode is used which contains the metal to be deposited and an electrolyte which contains a halogen compound of the metal to be deposited.

The electrolyte may consist of a salt melt or a solution in which is dissolved a halogen compound of the metal to be deposited. In most cases a mother melt is used consisting of one or more salts of metals which are more electropositive than the metal to be deposited. The mother melt contains the halogen compound. If it is a question of producing an alloy in the powdered form the mother melt may contain two or more halogen compounds of metals to be deposited. For practical and economic reasons it is usual to use a mother melt consisting of a mixture of sodium and potassium chloride.

The anode may consist of the metal to be deposited or, if it is a question of producing an alloy in the powdered form, of two or more metals. The anode may also consist of or contain a reducible compound of the metal to be deposited or, if it is a question of producing alloys in the powdered form, of two or more such compounds. In addition to the reducible compound or compounds the anode may also contain one or more reducing agents, preferably admixed with the reducible compounds. In the electrolytic process the metal compound is decomposed into metal and a gaseous residue, for example O_2, CO or CO_2.

The expression iron as used here and in the appended claims is understood to include, whenever applicable, alloys or other combinations of two or more metals in which iron is the base. Thus when in the following reference is made to the deposition of a metal this is intended to include deposition of a single metal as well as an allow. When reference is made to an anode containing or consisting of a metal this is intended to convey that the anode contains or consists of a single metal as well as that it contains or consists of an alloy or some other combination of two or more metals. The alloying components to be contained in the powder produced may all be contained in the same anode or divided between two or more anodes. One or more of the alloying components, but not all of them, may also be supplied to the electrolyte in other ways.

The expression "in the powdered form" is intended to cover also a form which is easily pulverizable.

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The expression "in the gaseous form" also includes "in the vaporous form."

For the sake of simplicity part of the following description will deal with the case that a single anode is used which consists of iron, that the electrolyte consists of a melt of sodium chloride to which iron chloride has been added, and that iron is to be deposited in the powdered form on or at the cathode. The invention is, however, not in any way limited to this specific example.

Reference will be made to the accompanying drawings in which Figure 1 shows a diagram, described more fully in the following, and Figure 2 an apparatus used for the carrying out of the process of the invention.

In practice, the carrying out of the electrolysis described presents certain difficulties and therefore certain investigations have been made particularly as to the iron concentration in the bath (or generally the concentration in the bath of the metal or metals to be deposited). The results obtained are illustrated in the diagram shown in Figure 1. In the diagram, the ordinate indicates the potential or voltage of the bath and the abscissa the iron concentration in the melt. The curve indicates how the potential of the bath varies with the iron concentration.

It is now desirable that the electrolytic process should be confined to a certain part of the curve. If the concentration of iron in the bath is too low or too high the process is disturbed.

If the iron concentration is too low, that is lower than about 0.1%, the voltage increases and also the power consumption. In addition the iron powder is obtained in a very finely divided form and as a rule cannot be used for powder metallurgical purposes as it does not flow very easily, has a low volumetric weight and only with difficulty can be compressed to a high degree of density.

In order to avoid these difficulties it has generally been recommended to add large amounts of iron chloride to the bath. High iron concentrations are, however, disadvantageous from the point of view that the iron chloride is unstable and volatilizes at relatively low temperatures. This also applies to most halides of the metals belonging to groups 4–8 in the periodic system. Sublimation and decomposition therefore cause considerable losses. The metal halides are also as a rule difficult to produce in the pure, anhydrous state. When they are added to the melt a considerable amount thereof is immediately

sublimated or decomposed, so that only a small part is dissolved in the melt.

Whether the iron concentration is low or high the concentration of sodium in the melt is finally increased to a point where the solubility of the sodium is exceeded and the sodium is precipitated. The explanation is that by and by iron chloride is sublimated from the bath which causes loss of chlorine.

In order to avoid these disadvantages it is therefore desirable to confine the process to a certain range of the curve shown in the diagram or, in other words, to control the iron concentration in the bath in a certain way. It has now been found that this can be done by introducing halogen into the bath in the gaseous form. For the purpose of the present invention "halogen" is understood to include halogen as such as well as suitable halogen compounds. It is thus possible to introduce into the electrolyte halogen as such, a hydrogen halogen compound or a halogen compound of a metal to be deposited. Instead of a halogen or a halogen compound it is possible to use two or more of each kind or mixtures of halogens and halogen compounds.

By controlling in this way the iron concentration in the electrolyte of the metal to be deposited it is possible to control the grain size of the metal deposited. Using an iron concentration of 2–5% in the melt, large and cubical crystals were obtained which were well suited for powder metallurgical purposes. By means of the method of the invention it is possible to obtain a product which wholly or to a very large part consists of the grain sizes most suitable for powder metallurgical purposes (for example by pressing and sintering). For powder metallurgical purposes it is often desirable to have a powder containing different grain sizes from 0.5 to 0.3 mm. and downwards. If the concentration in the melt of iron is decreased then also the size of the crystals deposited is decreased. On the other hand iron concentrations above 1–1.5% did not cause any considerable increase of the size of the product deposited. By means of the method of the invention it is therefore possible to control the grain size of the product deposited very accurately within certain limits. By controlling in this way the iron concentration in the electrolyte of the metal to be deposited it is possible to keep the voltage of the bath at so low a value that precipitation of more electropositive metals present in the electrolyte, for example sodium, or sodium and potassium, is prevented. It is further possible to keep the iron concentration within the limits which are set on the one hand by the rising bath voltage and on the other hand by the sublimation losses. By supplying the halogen in the gaseous form it becomes possible to obtain a very smooth and uniform control of the iron concentration.

The nature of the cathode is of minor importance. As an example may be mentioned that the cathode may be made of stainless steel. In the process of the invention the powder deposited on the cathodes adheres more strongly to the cathode than the powder deposits obtained by the ordinary methods. This is of advantage when separating the powder obtained from the electrolyte and above all from oxides or metalloid impurities contained in the melt or solution in the powdered form. It has further been found that the grains obtained, after washing and renewed reduction, are very soft and easy to deform, so that they easily form compacted bodies having a high degree of density. The controlled introduction of the halogen also serves to avoid explosions.

If the gas is introduced deep down into the melt or solution the absorption takes place more easily but the same result although as a rule slower, can be obtained by introducing the gas higher up in the melt or solution.

Due to the interdependence of the iron concentration to the bath voltage the introduction of the gas can be controlled automatically responsive to the potential difference between the anode and the cathode in such a way that gas is introduced or the supply of gas is increased when the potential difference increases. Thus if the introduction of the gas takes place intermittently the introduction of gas can be started when the potential increases above a certain value. If the introduction of the gas takes place continously the supply of gas can be increased when the potential increases above a certain value. The regulation of the gas supply can be carried out by means of known devices, the application of which is known to those skilled in the art. The gas may for example be introduced through a tube having a valve, and the valve may be operated by a voltage regulated device which when the voltage increases opens the valve or increases the supply of gas.

The supply of gas is preferably regulated so as to avoid precipitation of metals which require a higher discharge voltage than the metal to be deposited.

It has been found preferable to allow the electrolysis to proceed while the gas is being introduced but the same result, although slower, can be obtained if the electrolysis is interrupted while the introduction of the gas takes place.

The effect of the introduction of the gas is made evident by the potential between the anode and the cathode decreasing until a steady value is reached. This is due to the fact that precipitation is avoided of such metals, for example alkali metals, which require a higher discharge voltage than the metal to be produced.

The gas may be introduced into the electrolyte through a tube of a material which is indifferent to the gas. The gas may, however, also be introduced into the electrolyte in contact with and dissolving a metal to be deposited. Due to the high temperature at which the process is carried out the metal is attacked and passed into the electrolyte in the form of a halide. Instead of a single metal an alloy or any combination of two or more metals can be used in the same way. The alloy components are then introduced into the bath in the form of halides. The introduction of the gas can take place through a tube of a single metal, an alloy or any other combination of two or more metals. The metal in contact with which the gas is introduced may be contained in the anode. The anode may for example consist of or contain iron as such and the gas may be introduced through a tube of iron. It is, however, also possible to use an anode which contains at least two metals to be deposited and introduce the gas into the electrolyte in contact with and dissolving at least one but not all of the metals contained in the anode. In this way it is possible to control the composition of the deposit on the cathode. For example, if it is found that the deposition of a certain metal is too slow it is possible in this way to speed up the

deposition of this metal. As another example may be mentioned the case that an alloy consisting of three alloying components is to be produced. All of the alloying components may be contained in the anode and the gas may be introduced through a tube consisting of only one or two of these components; the gas may also be introduced through two separate tubes, one consisting of one component and the other of another component.

It is also possible to introduce the gas in contact with and dissolving a metal which is not contained in the anode. The anode may for example consist of iron and the gas be introduced through a tube of chromium, in order to produce an iron chomium alloy in the powdered form.

As will be seen from the above the gas may be introduced through a tube consisting of a single metal, a metal alloy or any other combination of two or more metals. The gas may, however, also be introduced through a tube, of an indifferent material or not, in which is placed in one form or another, as a metal or a metal compound, the metal or metals to be dissolved out in contact with the gas.

The introduction of the gas may also take place through canals in the anode.

The reactions taking place when halogen is introduced in one form or another are briefly as follows:

If Cl_2 is introduced through a tube of an indifferent material the chlorine with Na forms NaCl. The chlorine further, by attacking the anode or in other ways, forms $FeCl_2$.

If Cl_2 is introduced through a tube of metal the metal is dissolved to form $FeCl_2$ which is introduced into the electrolyte. Cl_2 also combines with Na.

If HCl is introduced the following reactions take place:

$$2Na+2HCl=2NaCl+H_2$$
$$HCl+Fe=FeCl_2+H_2$$

H_2 escapes from the bath.

If $FeCl_2$ is introduced the following reactions take place:

$$2Na+FeCl_2=2NaCl+Fe$$

Fe falls to the bottom of the electrolysis vessel,

$$FeCl_2 \rightleftarrows Fe+Cl_2$$

i. e. $FeCl_2$ is partly dissolved and dissociated.

Similar reactions take place when other metals and halogens or halogen compounds are used.

The melt baths or solutions may be neutral or alkaline. One embodiment of the invention is described more fully with reference to Figure 2 of the accompanying drawing.

The electrolytic cell A contains a molten bath B of NaCl and KCl. The cell is made of stainless steel and is by means of a conductor C connected with the negative pole of a direct current generator D. A suitable heating means for the cell can be used. F denotes an anode of iron immersed in the bath and by means of the conductor G is connected with the positive pole of the generator D. H denotes a tube of iron, also immersed in the bath so as to reach nearly to the bottom thereof. When the temperature of the bath reached 750° C. the generator was started and the voltage shortly after the beginning of the electrolysis was 4 volts. Immediately after the beginning of the electrolysis, violent combustion of metallic sodium took place at the surface of the bath at the cathode. This sodium is electrolytically deposited on the cathode and dissolved in the bath, and when the saturation point is reached, the sodium is precipitated from the bath and rises to the surface thereof owing to its low specific gravity. From the anode, iron is dissolved which in the bath pass to the cathode where they are deposited in extremely fine divided crystalline form, together with sodium. A slow stream of chlorine gas was introduced through the tube H. After the introduction of a few liters of chlorine gas, the deposition of metallic sodium on the cathode ceased and the cell voltage decreased to 1.9 volts. After 4 hours, the cell voltage had risen to 2.4 volts. Chlorine gas was then again introduced and the cell voltage again decreased to 1.9 volts. A sample of iron powder was removed from the bath and was found to have a grain size up to 0.5 mm. and a distribution of particle sizes which made it suitable for powder metallurgical purposes. No iron salts were added to the bath during the electrolysis except as formed as the result of the chlorine introduced attacking the iron of the iron tube. The concentration of the iron in the bath was maintained within the range 2–5%.

What I claim is:

1. In an electrolytic process for producing powdered iron in an electrolytic cell having an anode composed of iron and a cathode, the process comprising passing an electric current through an electrolyte between said anode and cathode, said electrolyte consisting essentially of alkali metal halide and ferrous chloride in the molten state, said current being of a density suitable for depositing iron on the cathode in the powdered form, maintaining the electrolyte at a temperature below the melting point of said iron to be deposited, introducing halogen into the electrolyte in gaseous form, and regulating the flow of halogen gas into said electrolyte at a level which maintains the concentration of said iron in the electrolyte so that the potential between the anode and cathode is below that at which metals which require a higher discharge voltage than iron are deposited, and limits the concentration of said iron in said electrolyte below that at which thermal decomposition of halides of iron takes place whereby metal of the desired grain size is produced.

2. In an electrolytic process for producing powdered iron in an electrolytic cell having an anode composed of iron and a cathode, the process comprising passing an electric current through an electrolyte between said anode and cathode, said electrolyte consisting essentially of alkali metal halide and ferrous chloride in the molten state, said current being of a density suitable for depositing iron on the cathode in the powdered form, maintaining the electrolyte at a temperature below the melting point of said iron to be deposited, introducing halogen into the electrolyte in gaseous form, and regulating the flow of halogen gas into said electrolyte at a level which maintains the concentration of said iron in the electrolyte between 0.1 and 5% so that the potential between the anode and cathode is below that at which metals which require a higher discharge voltage than iron are deposited, and limits the concentration of said iron in said electrolyte below that at which thermal decomposition of halides of iron takes place whereby metal of the desired grain size is produced.

3. In an electrolytic process for producing powdered iron in an electrolytic cell having an anode composed of iron and a cathode, the proc-

ess comprising passing an electric current through an electrolyte between said anode and cathode, said electrolyte consisting essentially of alkali metal halide and ferrous chloride in the molten state, said current being of a density suitable for depositing iron on the cathode in the powdered form, maintaining the electrolyte at a temperature below the melting point of said iron to be deposited, introducing halogen into the electrolyte in gaseous form in contact with iron, and regulating the flow of halogen gas into said electrolyte at a level which maintains the concentration of said iron in the electrolyte between 0.1 and 5% so that the potential between the anode and the cathode is below that at which metals which require a higher discharge voltage than iron are deposited, and limits the concentration of said iron in said electrolyte below that at which thermal decomposition of halides of iron takes place whereby metal of the desired grain size is produced.

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REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
1,861,625	Driggs	June 7, 1932
2,406,935	Wood et al.	Sept. 3, 1946
2,413,411	Kroll	Dec. 31, 1946

OTHER REFERENCES

Transactions of the American Electrochemical Society, vol. 47 (1925), pages 265–274; vol. 87 (1946) pages 551–566; vol. 89 (1946), pages 373–382.