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ELECTROLYTIC METAL POWDERS

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This invention relates to the production of metal powders and has for its principal object the provision of an improved electrolytic method of producing metal powders, particularly powders of certain of the so-called ferrous metals.

Attempts to produce metal powders by electrolytic means have been successful principally in the case of metals such as copper which are easily deposited at the cathode of an electrolytic cell and which are not particularly subject to contamination or corrosion during the course of the electrolytic operation. Ferrous metals, by which I mean the group consisting of iron, nickel and chromium, are not of this class, and attempts to produce these metals electrolytically in the form of powder have not heretofore been wholly successful.

In accordance with the present invention, a process is provided by means of which it is possible to produce substantially uncontaminated iron and other ferrous metal powders, for example, nickel powder or chromium powder, electrolytically. The process of the invention involves introducing metal-bearing material into an electrolytic cell comprising an anode, a cathode and an electrolyte, incorporating in the electrolyte a substance capable of promoting formation at the cathode of a substantially uncontaminated deposit of the metal in a form easily reducible to metal powder, and subjecting the metal-bearing material in the cell to an electrolytic operation. The metallic deposit which forms at the cathode during the course of the electrolysis is removed from the cell and, if necessary, is subjected to a grinding operation to produce a metal powder of the desired degree of fineness.

Several substances capable of promoting formation at the cathode of a substantially uncontaminated metallic deposit in a form easily reducible to metal powder are available. Sugar (particularly sucrose) and glycerine have been employed with some success. Urea has given especially satisfactory results. The substance employed is generally incorporated in the electrolyte before carrying out the electrolytic operation, but if desired some or all of the substance may be added at the commencement of or during electrolysis.

The electrolytic operation may be carried out using either soluble or insoluble anodes. If soluble anodes are employed, anodes containing a substantial proportion of the chosen metal, e. g. iron, nickel or chromium, are prepared and introduced into the electrolytic cell. When an electric current is passed through the cell, the metal dissolves from the anode and simultaneously a

corresponding quantity of the metal deposits at the cathode. If insoluble anodes are employed, a salt of the metal it is desired to obtain in powdered form (for example, a soluble salt of iron, nickel or chromium) is incorporated in the electrolyte and the metal is deposited therefrom at the cathode during electrolysis.

The cathodic deposit produced in accordance with the process of the invention may or may not be in the form of powder. Generally a substantial proportion of the deposit is formed directly as metal powder, but not infrequently some metal deposits on the cathode in the form of thin plates or flakes. Such plates or flakes are periodically stripped or scraped from the surface of the cathode and are subjected to a grinding operation to reduce them to a powder of the desired degree of fineness. Metal deposited directly as powder also may be subjected to the grinding operation in the event that the size of the individual particles of the powder are larger than desired.

The process of the invention is particularly well suited to the production of metallic iron powder. In the following description of a specific embodiment of the invention, therefore, particular reference is made to the production of iron powder, but it is understood that the description is illustrative in character and is not to be construed as limiting the scope of the invention.

If the process is to be carried out using soluble anodes, the anodes are prepared from the metal it is desired to obtain in powdered form. In the case of iron, the anodes consist principally of metallic iron. The iron employed in making the anodes should be reasonably pure. Iron containing a large proportion of carbon, sulphur or phosphorus is not desirable, for such impurities find their way into the cathodic deposit formed during the electrolysis and contaminate the iron powder product. Consequently mild steel containing one or two tenths of a percent of carbon and little or no sulphur or phosphorus are better suited for use in the process as the iron-bearing material than are most of the common cast or pig irons. A particularly satisfactory source of iron-bearing material is the iron residue from detinning operations. So-called "tin" cans are usually made from a good grade of soft steel, and this steel, after the lead and tin employed at soldered seams in the cans and tin in the form of plate has been removed, is very well adapted for use in the process.

After the anodes have been suitably prepared, they are placed in an electrolytic cell containing an electrolyte. The electrolyte preferably con-

tains a salt of the metal intended to be deposited during the course of the electrolytic operation; for best results in producing iron powder, an iron salt is employed. Ferrous salts are preferable to ferric salts; because in any event it will be necessary to have the salt in the ferrous state before deposition of metallic iron at the cathode can occur. If ferric salts are employed, some current must be expended during electrolysis to reduce the salt to the ferrous state, whereas this is avoided if ferrous salts are used in the first instance.

Aqueous solutions of a number of salts have been employed with varying degrees of success as the electrolyte in the production of iron powder. For example, iron salts of citric acid, tartaric acid and oxalic acid in water have been used. Sodium thiosulphate in aqueous solution, when used as the electrolyte, results in the production of iron powder at the cathode, but the deposit is contaminated to some extent with sulphur. Ferrous ammonium sulphate dissolved in water in a concentration of about 350 grams per liter gives a satisfactory electrolyte. An aqueous solution of ferrous sulphate, however, has been found to be most satisfactory. The ferrous sulphate is used in a concentration of about 250 grams $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ per liter. Advantageously a small quantity of sulphuric acid is added to the electrolyte, say two cubic centimeters of concentrated sulphuric acid per liter of ferrous sulphate solution.

If the ferrous sulphate solution alone is used, insoluble ferric salts tend to form and metal deposited at the cathode is contaminated by oxidation. To some extent this difficulty may be overcome by lowering the current density, but this in turn leads to difficulties of another sort: at lower current densities the iron deposited is quite malleable and not suited for reduction to the state of powder. To overcome these difficulties, a substance capable of promoting formation of a substantially uncontaminated deposit of iron in a form easily reducible to iron powder is added to the electrolyte. Cane sugar (sucrose) and glycerin have been employed with some success, but most satisfactory results have been secured using urea. The urea is dissolved in the electrolyte, preferably prior to commencement of the electrolysis. The concentration of urea in the electrolyte should amount at least to about three percent by weight; if less than three percent is employed, oxidation of the iron salts is not effectively inhibited.

Various other substances may be added to the electrolyte to improve the efficiency of the electrolysis and the character of the cathodic deposit. Sodium and ammonium salts, if added to the electrolyte, increase the conductivity thereof and thereby lower the consumption of power during the electrolysis. Zinc sulphate and other zinc salts in the electrolyte improve the character of the deposit and increase the yield of cathodic iron, but should not be employed in very high concentrations or the deposited iron will be contaminated with zinc.

The character and quality of the deposit formed at the cathode is dependent to some extent on the material of which the cathode is composed. Either iron or zinc may be employed, but considerably better results are obtained using a zinc cathode. The cathode is spaced about five centimeters from the anode for most satisfactory results, but this spacing may be varied within limits without seriously impairing the efficiency of the

operation or the character of the cathodic deposit. If desired, a permeable diaphragm may be interposed between the anode and cathode to prevent migration of ferric hydroxide and other oxidized cell products to the cathode, but this precaution is not ordinarily necessary.

In carrying out the electrolysis, an electric current is passed from anode to cathode through the electrolytic cell. The cell voltage amounts to about 5 with a current density of about 8 amperes per sq. dm. (75 amperes per sq. ft.). The soluble iron anode is gradually dissolved during the course of the electrolysis and simultaneously a deposit of metallic iron forms at the cathode. The deposit is, to a considerable extent, quite finely divided and may be withdrawn from the cell and employed as iron powder for many purposes without further treatment. Generally a portion of the deposit is in the form of brittle flakes or plates adhering to the cathode; and the iron so deposited is subjected to a grinding operation to produce iron powder of the desired degree of fineness.

The grinding operation may be carried out in any suitable manner, for example, in a disintegrator, a ball mill, a rod mill, a pebble mill, or any one of the common grinding machines for reducing substances to powder form. If a ball mill is employed, it may be desirable to employ hard-faced or chromium plated balls in order to avoid contamination of the iron powder with the material of which the balls are made.

Below are given the data of two experiments, carried out in accordance with the invention, which resulted in the production of a cathodic deposit of iron in a form easily reducible to iron powder.

	Experiment No. 1	Experiment No. 2
Electrolyte, grams/liter:		
$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	248	248
H_2SO_4	2 cc.	2 cc.
Cane sugar.....	12.5	12.5
Urea.....		12.5
Anode material.....	Iron	Iron
Number of anodes.....	2	2
Anode area, sq. cm.....	240	240
Original weight anode, grams.....	491	512
Final weight anodes, grams.....	420	454
Anode weight loss, grams.....	71	58
Cathode material.....	Rolled Zn	Rolled Zn
Number of cathodes.....	1	1
Cathode area, sq. cm.....	240	240
Original weight cathode, grams.....	67	68
Final weight cathode, grams.....	79	74
Cathodic weight gain, grams.....	12	8
Weight powder in bottom of cell, grams.....	68.3	65.5
Total cathodic deposit, grams.....	80.3	73.5
Anode-cathode distance, cm.....	5	5
Diaphragm.....	None	None
Volume of electrolyte, cc.....	2000	2000
Temperature, °C.....	56	67
Total current, amperes.....	19.5	19.5
Current density, amps./sq. dm.....	8.1	8.1
Voltage, average.....	5.0	4.5
Time of electrolysis, hours.....	4.25	4.25
Approximate current efficiency, per cent.....	92.7	84.9
Kwh. per lb. iron.....	2.34	2.29

The process of the invention is susceptible to various modifications. In the foregoing description, particular reference has been made to the use of soluble anodes, but insoluble anodes may also be employed. Lead is a satisfactory material from which to make insoluble anodes, but other materials also may be employed. The electrolyte is of substantially the same composition when using insoluble anodes as when using soluble anodes, that is, it advantageously comprises an aqueous solution of ferric sulphate or other metal salt in which urea or other substance capable of promoting formation of a cathodic deposit

in a form easily reducible to metal powder has been incorporated. The iron or other metal is deposited from the solution and of course some provision must be made to add more iron to the electrolyte as it becomes depleted in iron during the course of the electrolysis. The make-up iron may be added continuously or intermittently. Advantageously the electrolyte is continuously withdrawn from the cell, make-up iron is added to it (preferably by dissolving metallic iron in the now acidic electrolyte) and the replenished electrolyte is returned continuously to the cell at substantially the same rate at which depleted electrolyte is withdrawn.

The process of the invention leads to the production of a high-grade, very finely divided metal powder. Iron powder produced in accordance with the invention is of very high grade, containing upwards of 99.5% Fe. The particle size of the powder is adequately small for practically all powder metallurgy applications. Screen analyses of powder produced in accordance with the invention gives the following results:

	Per cent
—400 mesh-----	25
200 to 400 mesh-----	25
+200 mesh-----	50

If carefully prepared, 100% will pass through a 100 mesh screen.

To a considerable extent the efficiency of the process is attributable to incorporation of urea or equivalent agent in the electrolyte. The urea functions primarily to inhibit oxidation of the cathodic deposit, but it appears also to have some influence on the character of the deposit. The character of the deposit is also affected by the current density employed. At high current densities, a very brittle deposit is formed, while at low current densities a malleable deposit appears on the cathode. It is therefore possible to employ the process of the invention in electrolytic operations having for its object the production of metal sheets or plates suitable for rolling or other working. The only modification necessary in carrying out the process with this end in view is to employ lower current densities than when seeking a deposit suitable for reduction to powder form.

We claim:

1. The method of producing iron powder which comprises introducing iron-bearing material into an electrolytic cell comprising an anode, a zinc cathode and an aqueous electrolyte containing ferrous sulphate, incorporating in the electrolyte at least one soluble organic substance selected from the group consisting of sugar, glycerine and urea, and subjecting the iron-bearing material in the cell to an electrolytic operation at a relatively high current density.

2. In a method of producing iron powder in which an electric current is passed through an aqueous solution of an iron salt to form a cathodic deposit of the iron, the improvement which comprises conducting the electrolysis of the solution in the presence of a water-soluble or-

ganic compound selected from the group consisting of sugar, glycerine and urea, and maintaining a relatively high current density substantially in excess of that at which the metal tends to deposit in malleable form passing through the solution containing the substance selected from the group.

3. In a process for producing iron powders in which an iron-containing solution is subjected to electrolysis to deposit the iron from the solution, the improvement which comprises subjecting an aqueous solution of an iron salt selected from the group consisting of citrates, tartrates, oxalates, thiosulphates and sulphates to electrolysis at a current density substantially in excess of that at which a malleable massive deposit of iron is formed in the presence of at least one agent selected from the group consisting of sugar, glycerine and urea, whereby the deposited iron tends to be brittle and finely divided and hence easily reducible to powder form.

4. In a process for producing iron powder in which a solution containing iron is subjected to electrolysis to deposit iron from the solution, the improvement which comprises conducting the electrolysis at a high current density substantially in excess of that at which the iron deposits in malleable massive form in the presence of substantial proportions of an iron sulphate and at least one agent selected from the group consisting of sugar, glycerine and urea, whereby the deposited iron tends to be brittle and finely divided and hence easily reducible to powder form.

5. In a process for producing powders of iron in which a solution containing the iron is subjected to electrolysis to deposit the iron from the solution, the improvement which comprises subjecting a solution of ferrous sulphate to electrolysis at a current density in the neighborhood of 75 amperes per square foot of cathode area in the presence of urea whereby the deposited ferrous metal tends to be brittle and finely divided and hence easily reducible to powder form.

6. The method of producing iron powder which comprises subjecting an aqueous electrolyte containing ferrous sulphate to electrolysis at a high current density in the presence of at least one soluble organic substance selected from the group consisting of sugar, glycerine and urea.

7. In a process for producing iron powders in which a solution containing the iron is subjected to electrolysis to deposit the iron from the solution, the improvement which comprises subjecting a solution containing about 250 grams $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ per liter to electrolysis at a cathode current density of about 75 amperes per square foot, said electrolysis being conducted in the presence of a compound selected from the group consisting of glycerine, sugar and urea.

8. Process according to claim 7, characterized in that the solution subjected to electrolysis contains a substantial proportion of sulphuric acid.

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