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ELECTROLYTIC IRON FOR POWDER METALLURGY PURPOSES

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This invention relates to the electrolytic production of iron which is particularly adapted for iron powder metallurgy purposes.

In the common electrodeposition processes such as copper plating, nickel plating and chromium plating methods, it is desired that the deposited metal adhere firmly to the cathode and that it possess such characteristics that the deposited metal forms a protective coating over the cathode. In the electrolytic deposition of metals such as iron in which the deposited metal is to be used for powder metallurgy purposes, the deposited metal should be preferably quite brittle and have a low ductility so that it may be readily removed from the cathode and may be easily reduced to a powder form as distinguished from a flaky form common to aluminum powder. The powder form is desired so that the reduced material flows readily in automatic machines used to introduce the powder into dies.

One of the purposes of this invention is to provide an improved method for the production of electrolytic iron for powder metallurgy purposes.

A further object of this invention is to provide an improved eletrolytic bath for the production of iron for iron powder metallurgy purposes.

A further object of this invention is to provide an improved method and an improved electrolytic bath for the production of electrolytic iron having a high degree of brittleness and a low ductility.

Another object of this invention is to provide a method and an electrolytic bath for the production of eletrolytic iron whereby the power consumption per unit weight of iron is relatively low.

Other objects and advantages of this invention will become apparent from the description and claims which follow.

The present invention contemplates the electrolysis at high current densities of an electrolytic bath containing ferrous chloride, ammonium sulphate and ferrous sulphate.

Electrolytic iron baths containing ferrous chloride, ammonium sulphate and ferrous sulphate have been known and have been used in the prior art. The ratio of ferrous chloride to ammonium sulphate to ferrous sulphate has been about 1:1.2–1.6:2. The cathode current density employed in the electrolysis of these baths usually has been held within a range of from about 10 to about 15 amperes per square foot.

I have discovered that iron may be deposited in a more brittle and friable condition and with a lower degree of adherence to the cathode by

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substantially increasing the relative proportions of ammonium sulphate and ferrous sulphate and by employing substantially higher cathode current densities. The deposited iron may be readily removed from the cathodes by a sharp blow with a hammer operated either manually or by power. The deposited iron made in accordance with my invention is extremely hard and brittle and may be readily ground into the desired powder form. This powder flows freely and may be advantageously employed in automatic feeding apparatus.

I have discovered that the desired type of deposit may be obtained from electrolytes in which the ratio of ferrous chloride, $FeCl_2.4H_2O$, to ammonium sulphate, $(NH_4)_2SO_4$, to ferrous sulphate, $FeSO_4.7H_2O$, lies in the range of from 1:7:9 to 1:23:32, the amount of each of the salts being expressed as parts by weight in solution. The total iron content of the electrolyte preferably varies between about 25 grams to about 40 grams per liter of electrolyte. The pH of the electrolyte is preferably maintained at about 3.0 or slightly below the hydrogen ion concentration at which the ferric hydroxide would be precipitated. This degree of acidity also aids in the production of hydrogen at the cathode which is adsorbed by the iron or which forms unstable hydrides with the iron. The impregnation of the deposit with hydrogen and the possible formation of the unstable hydrides aids in producing a friable iron deposit having a high degree of brittleness. Too large an excess of free acid is undesirable because the electrolysis of the large excess of acid increases the power consumption required per unit weight of deposited metal without any apparent improvement in the properties of the deposited metal.

The cathode current density may be varied over a considerable range and I have successfully employed cathode current densities as high as about 375 amperes per square foot. When employing these high current densities a higher power consumption results because of the heat loss occasioned by the excessive heating of the electrolyte and the increased production of hydrogen at the cathode. In most instances where the higher current densities are employed it is necessary to cool the electrolyte and I prefer to maintain the temperature of the electrolyte below about 50° C. but above the temperature at which the salts precipitate. Temperatures substantially exceeding 50° C. appear to result in the deposit of iron having a lower degree of brittleness. In the practice of my invention I

prefer to use current densities of the order of 70 amperes per square foot of cathode area. Since the cathode area increases as iron is deposited upon the cathode I prefer to employ an initial current density of about 70 amperes per square foot and maintain an actual cathode current density during the deposition of at least 30 amperes per square foot of cathode surface. At these current densities it is usually not necessary to cool the electrolyte.

Any desired types of anodes may be employed. In the practice of this invention I have found that scrap iron, steel rails and the like will produce satisfactory iron for iron powder metallurgy. Where the iron powder is desired in a relatively pure state the anode should be of relatively pure iron. When steel anodes are employed the carbon will eventually contaminate the bath and this carbon may be removed periodically or continuously by filtering the electrolyte.

The deposit may be allowed to build up to any desired thickness on the cathodes and the cathodes then removed from the electrolyte. The deposited iron is removed from the cathode as by hammering and then reduced to powder form as by ball milling or hammer milling. The hydrogen, present either as adsorbed hydrogen or in the form of iron hydrides or both, and oxygen may be removed by heating the powder to temperatures of from about 750° to about 900° C. in an atmosphere of hydrogen.

Iron baths containing ferrous chloride and ferrous sulphate have been considered somewhat difficult to control on the anode side. I have discovered, however, that if the relative proportions of the salts are maintained within the ratios set forth herein, there appears to be no difficulty in controlling this electrolyte. Ordinarily, chloride baths may be operated at appreciably higher cathode current densities than sulphate baths but oxidize more readily than sulphate baths. By preparing baths in accordance with my invention it is possible to use high current densities as in chloride baths and also inhibit the oxidation of the electrolyte as in sulphate baths.

I have produced electrolytic iron of the desired properties from a number of different baths having compositions within the range set forth herein. In general the electrolytic iron has been produced with a rather low power consumption.

As illustrative of this invention the following specific examples are set forth:

Example 1

A bath was prepared having the following composition per liter of solution:

	Grams
Ferrous chloride ($FeCl_2.4H_2O$)	18
Ammonium sulphate	140
Ferrous sulphate ($FeSO_4.7H_2O$)	175

Mineral acids such as hydrochloric acid or sulphuric acid may be added to lower the pH of the solution to about 3.0 and, as the bath is operated, additional quantities may be added from time to time to maintain the electrolyte at such value. In this example, as well as those which follow, scrap angle iron was employed as the anode material. The cathodes were iron rods. During the electrolysis the actual cathode current density varied because of the gradual increase in cathode surface area as the iron was deposited. The initial current density, therefore, was higher than the cathode current density at the time the electrolysis was discontinued. An approximate average of the current density is therefore used in arriving at the power consumption.

The power consumption employing an average cathode current density of about 70 amperes per square foot of cathode area was about 0.81 kilowatt hour per pound of iron produced. When employing an average cathode current density of about 85 amperes per square foot the power consumption was about 0.68 kilowatt hour per pound of iron produced.

Example 2

An electrolyte was prepared having the following composition per liter of solution:

	Grams
Ferrous chloride ($FeCl_2.4H_2O$)	4.5
Ammonium sulphate	101
Ferrous sulphate ($FeSO_4.7H_2O$)	142

This bath was brought to a pH of about 3.0 by the addition of sulphuric acid and was maintained at such value by periodic additions of acid. Electrolysis of this bath at an average cathode current density of about 70 amperes per square foot of cathode area resulted in a power consumption of about 0.5 kilowatt hour per pound of iron produced. When an average cathode current density of about 34 amperes per square foot of cathode area was employed the power consumption was about 0.62 kilowatt hour per pound of iron produced.

The deposited iron was highly brittle and of a low ductility. A sharp blow from a hammer fractured the deposit which fell from the cathode. This material was then reduced to powder by ball milling or hammer milling. The resulting powder appears amorphous and is in the form of cleanly broken elongated grains rather than flattened grains or flakes as is common to aluminum powder. The powder may be annealed in a hydrogen atmosphere at temperature of from 750° to 900° C. so as to remove oxygen and hydrogen. Such powder is admirably suited for powder metallurgy purposes.

It is to be understood that the specific examples are set forth merely as illustrative of my invention and are not intended as limitatitons of the invention.

I claim:

1. An electrolyte for the electrodeposition of iron for powder metallurgy purposes consisting essentially of an aqueous solvent and a solute of ferrous chloride, ammonium sulphate, ferrous sulphate and a small amount of acid, the ferrous chloride, ammonium sulphate and ferrous sulphate being in the ratio of about 1:7:9 to about 1:23:32, the electrolyte containing, in solution, from about 25 grams to about 40 grams of iron per liter, the amount of acid being sufficient to maintain the pH slightly below the hydrogen ion concentration to which ferric hydroxide is precipitated.

2. An electrolyte for the electrodeposition of iron for powder metallurgy purposes consisting essentially of an aqueous solvent and a solute of ferrous chloride, ammonium sulphate, ferrous sulphate and a small amount of acid, the ferrous chloride, ammonium sulphate and ferrous sulphate being in the ratio of about 1:7:9 to about 1:23:32, the amount of acid being sufficient to maintain the bath at a pH of about 3,0, the electrolyte containing, in solution, from about 25 grams to about 40 grams of iron per liter.

3. The method of preparing electrolytic iron for powder metallurgy purposes which comprises maintaining a bath consisting essentially of an

aqueous solvent and ferrous chloride, ammonium sulphate and ferrous sulphate in the ratio of about 1:7:9 to about 1:23:32, and an amount of acid sufficient to maintain the pH slightly below the hydrogen ion concentration at which ferric hydroxide is precipitated, electrolyzing the bath with a cathode current density of from about 30 amperes to about 375 amperes per square foot, the electrolyte containing, in solution, from about 25 grams to about 40 grams of iron per liter and reducing the deposited iron to powder form.

4. The method of preparing electrolytic iron for powder metallurgy purposes which comprises maintaining a bath consisting essentially of an aqueous solvent and ferrous chloride, ammonium sulphate and ferrous sulphate in the ratio of about 1:7:9 to about 1:23:32, and an amount of acid sufficient to maintain the pH slightly below the hydrogen ion concentration at which ferric hydroxide is precipitated, electrolyzing the bath with a cathode current density of from about 30 amperes to about 70 amperes per square foot while maintaining the temperature of the electrolyte below 50° C., and above the temperature at which the salts precipitate, the electrolyte containing, in solution, from about 25 grams to about 40 grams of iron per liter and reducing the deposited iron to powder form.

5. The method of producing electrolytic iron for iron powder metallurgy purposes which comprises maintaining a bath consisting essentially of an aqueous solvent and ferrous chloride, ammonium sulphate, ferrous sulphate and sulphuric acid, the ratio of ferrous chloride, ammonium sulphate and ferrous sulphate being about 1:7:9 to about 1:23:32, the amount of acid being sufficient to maintain the solution at a pH of about 3.0, electrolyzing the bath with a cathode current density of from about 30 amperes to about 375

amperes per square foot, the electrolyte containing, in solution, from about 25 grams to about 40 grams of iron per liter and reducing the deposited iron to powder form.

6. The method of producing electrolytic iron for iron powder metallurgy purposes which comprises maintaining a bath consisting essentially of an aqueous solvent and ferrous chloride, ammonium sulphate, ferrous sulphate and sulphuric acid, the ratio of ferrous chloride, ammonium sulphate and ferrous sulphate being from about 1:7:9 to about 1:23:32, the amount of acid being sufficient to maintain the solution at a pH of about 3.0, electrolyzing the bath with a cathode current density of from about 30 amperes to about 70 amperes per square foot while maintaining the temperature of the bath below 50° C. and above the temperature at which the salts precipitate, the electrolyte containing, in solution, from about 25 grams to about 40 grams of iron per liter and reducing the deposited iron to powder form.

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