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ELECTROLYTICALLY DEPOSITED IRON PRODUCTS

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This invention relates to electrolytically deposited brittle iron plate and the powders and cold die pressed bodies formed from such plate. The present application is a continuation in part of my application for Letters Patent of the United States, Serial No. 611,947, filed August 22, 1945, which is a continuation-in-part of my application Serial No. 560,783, filed October 28, 1944, now abandoned.

The principal objects of my invention are:

1. To provide a low cost iron deposit which is characterized by the presence of a sufficient quantity of oxide and hydroxide of iron to render the product readily grindable to particles of sizes suitable for use in iron powder metallurgy and from which the hardening constituents may be readily removed by simple annealing treatment.

2. To provide a brittle iron plate which may be ground economically to minus 325 mesh sizes and of such equiaxial particle shapes as to form in the subsequent annealing treatment porous clusters of particles which remain as porous clusters after the final crushing and screening operations.

3. To provide an electrolytically deposited, porous, brittle iron plate which adheres well to the cathodes during deposition.

4. To provide an iron powder which in structure and composition is superior to the products of this kind heretofore produced for use in cold die pressing operations.

5. To provide an iron powder which is characterized by its good flow rate, uniform screen size distribution, uniform apparent density and high green strength when compacted preparatory to sintering, combined with a high degree of purity, i. e., above 99.5%.

6. To provide an iron powder which is particularly adapted to receive conventional cold die pressing and sintering treatment to form bodies having high tensile strength and good elongation, due to the uniformity of composition and improved grain structure, substantially devoid of planes of weakness.

7. To provide iron powders having apparent densities which are controllable within narrow limits not exceeding 0.1 gram per cc. thereby affording uniformity in the compression ratio and greatly facilitating standardized compacting operations.

8. To provide iron powders in the form of particles of controlled mesh sizes and of such purity, softness and structure that the compacted articles formed therefrom do not expand appreciably or substantially when the pressure is removed preparatory to sintering and also of

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such composition that the compacts do not shrink substantially as a result of the sintering treatment.

Other objects will appear and be more fully pointed out in the following specification and claims.

My improved iron products may be electrolytically deposited as described and claimed in my application Serial No. 660,039, filed April 6, 1946, or in accordance with my application Serial No. 611,947, filed August 22, 1945, hereinbefore referred to. In accordance with either process it is essential that the conditions present in the deposition cells with respect to (1) solution composition, (2) current density of the deposition and (3) temperature of deposition, shall be controlled and maintained within the limits presently to be described. The range of permissible values from a technical standpoint must be further limited to minimize the cost of production and facilitate control in commercial operations.

Solution composition

An electrolyte comprising a ferrous chloride solution has been found best suited for my purposes. The limits of the solution concentration are interrelated with those of the temperature and current density of deposition. For example, the upper limit of iron concentration, as ferrous chloride, in the solution is somewhat dependent on the lowest temperature which can be economically maintained in the cell. If, as in most installations, it is not economical to keep the deposition temperature below 15 degrees C. the maximum concentration of iron is approximately 125 grams per liter for dull iron plate deposition. It is, however, much more economical to keep the iron concentration below this figure and I have found for most economical operation that the iron in solution should be maintained at between 50 and 75 grams per liter. With more dilute solutions it is necessary to increase the voltage in order to obtain a given current density of deposition and this progressively increases the power consumed per pound of iron deposited. It is feasible, however, to obtain dull iron plate with maximum solution concentrations ranging from about 67 to 86 grams of iron per liter where the current densities range from about 10 to 40 amperes per square foot and temperatures at or below 25 degrees C. are maintained in the cells.

A further necessary control involves hydrogen ion concentration of the solution. Its pH should be maintained between 3.0 and 5.5. A pH lower than 3 indicates the presence of excessive acid

or ferric chloride and results in a bright iron cathode deposit which is unsuited for my purposes and is otherwise not satisfactory because of its poor adherence to the cathode plates. In practice the pH of my solution naturally adjusts itself between 5 and 5.5. With pHs above 5.5 the solution tends to hydrolyze and a deficiency of iron in solution develops under conditions indicated by substantially higher pH values. The presence of ferric chloride in the solution is neither desirable nor necessary for the functioning of my process. Other additions to the electrolyte, such as ammonium chloride and calcium chloride which have been used heretofore, are also detrimental.

The electrolyte for use in my process may be obtained by dissolving scrap iron, preferably of low carbon content, in hydrochloric acid. This concentrated solution of ferrous chloride is diluted so that it contains iron within the limits hereinbefore described and preferably about 60 grams of iron, as ferrous chloride, per liter of solution.

Current density

In order to produce my dull iron plate economically, the current density between electrodes of the deposition cells must be maintained between certain values which are interdependent upon the concentration of iron in solution and temperature of deposition. In general, the higher the solution concentration the greater must be the current density at any given temperature within the feasible range. As hereinbefore indicated, practical limits of the current density are from about 10 to 40 amperes per square foot where the solution concentration ranges from a maximum of about 67 to 87 grams of iron per liter of solution and where a temperature at or below 25 degrees C. is maintained in the cell. The power consumed per pound of iron deposited increases in direct proportion to the current density and in inverse proportion to the temperature of deposition.

Temperature of deposition

In order to produce dull iron plate most economically the temperature of deposition should be maintained between 15 degrees and 35 degrees C. and preferably at approximately 25 degrees C. where the economical ranges of current densities and solution concentrations hereinbefore described are maintained. An unsatisfactory, bright, malleable deposit results when a temperature substantially above 40 degrees C. is reached in a cell of the character described.

Cells and electrodes

My process may be carried out in inexpensive open cells without diaphragms between the anodes and cathodes. In accordance with my application Serial No. 660,039, ingot iron plates of suitable thickness, preferably about one-half inch thick, may be used as the electrodes in the cells. These plates may contain up to .2% of carbon and substantial amounts of other impurities. For example, they may contain .03% carbon together with manganese, silicon and sulphur totaling approximately .10% and copper approximately .15%. Such electrodes are placed in spaced, parallel, electrical series arrangement in the cells and for maximum anode recovery are completely submerged in the electrolyte. They are preferably spaced from two to three inches, center to center, and furnished preferably in sizes that can be

handled without the aid of power driven hoists, cranes or conveyors.

To control the temperature of deposition, inexpensive heat exchangers may be placed in the cells or built into the walls of the same, or the electrolyte may be circulated through a heat exchanger located exteriorly of the cells.

Direct current conductors are connected respectively to the end electrodes of each cell and current is passed at the required voltage through the electrodes in series each of them constituting a soluble anode at one face and receiving a cathode deposit on its opposite face. At the start of the electrolysis, all electrodes are alike and they may comprise ingot iron plates or other inexpensive iron plates containing impurities as hereinbefore described. Either of the end electrodes may act as a soluble anode and the other as a cathode depending on the direction of flow of current.

During the electrolysis, the concentration of the electrolyte is maintained as described and its pH tends to remain at its required value of from 3 to 5.5. Periodically, if necessary, a small amount of hydrochloric acid may be added. A cell temperature below 40 degrees C. is maintained and current at the density required, preferably from 16 to 18 amperes per square foot, is passed between electrodes in the series arrangement so that the metal from the positive face of each electrode goes into solution and is re-deposited on the negative face of the electrode adjacent to it. The electrolysis may be continued until all of the electrodes have been converted into electro-deposited iron of the desired dull gray and porous character. This product is subsequently subjected to the successive grinding, annealing, regrinding and screening to produce my improved powders.

Further details of my series deposition process for forming dull iron plate are herein included by reference to my application Serial No. 660,039.

As an alternative, the electrically parallel arrangement of electrodes in the cells, more fully described in my application Serial No. 611,947, may be employed. Accordingly, the electrodes may be provided individually with leads extending to bus bars along opposite sides of the cell and the anodes may comprise ingot iron plates of suitable thickness, preferably from one-half to one inch thick and may contain up to .2% carbon and substantial amounts of other impurities. As the cathodes from which the dull iron plate may be removed periodically and with ease, flexible cathode starting sheets comprising stainless steel, for example, that contains 18% chromium and 8% nickel may be used. Sheets of $\frac{1}{16}$ inch to $\frac{1}{8}$ inch thickness have been found to be adequately stiff to remain straight in the cells while affording the flexibility necessary for removal of the brittle iron deposit. The electrolyte for use in the parallel arrangement of anode and stainless steel cathode starting sheets may be obtained by dissolving scrap iron as hereinbefore described and may be diluted so that it contains iron within the limits specified and preferably between 50 and 75 grams of iron per liter. The cells are cooled to maintain a temperature of electrolyte therein below 40 degrees C. Where anode plates of approximately one inch thickness are used they may be spaced about two inches, center to center, relative to the adjacent stainless steel cathode sheets. The current is supplied at a voltage such that there is a voltage drop between adjoining electrodes within the range 1.5 to 2 volts. Direct

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current from a motor generator set or from other source, such as a rectifier may be employed. The required pH, 3 to 5.5, current density between 5 to 40 amperes per square foot and preferably at approximately 30 amperes per square foot are maintained during the deposition.

In operation, from time to time as iron is deposited on the stainless-steel cathode sheets, these sheets are removed from the cell and flexed to dislodge the brittle, dull iron deposit after which they may be replaced in the cell to receive a further deposit of iron. Separation of the iron plate from the cathode sheets is facilitated if the coating is allowed to accumulate to a thickness of from $\frac{1}{8}$ to $\frac{1}{4}$ inch. The flexing of the iron coated sheets may be performed manually by bending the sheets over a roller or bar, or otherwise in a machine designed for the purpose. It may be necessary to clean the cathode sheets periodically and this may be accomplished by dipping them in dilute hydrochloric acid for a period of from one to five minutes. Cathode sheets of the character described are so durable that they may be used almost indefinitely. The anode plates are merely replaced by new ones periodically as they are dissolved in the electrolyte. Other details of the operation are well known in this art and require no further explanation.

By maintaining the preferred conditions hereinbefore described in the cells, I obtain a porous, brittle, coherent, dull iron deposit with current efficiencies above 100%. The reasons for this amazingly high efficiency are not entirely clear but it is thought that it is at least in part due to the porosity and coherent nature of my cathode deposit. The outer layer of iron as it is formed may act as an intermediate electrode between the anode plate and cathode sheet and electrolysis may cause decomposition of water in the pores between this outer layer and the cathode sheet whereby hydrogen and oxygen are liberated in these pores. Since the outer layer is iron in a very pure form it may combine with the liberated gases to form iron oxide and hydroxide under the conditions existing in the cell. Accordingly, current efficiencies above 100% may indicate that the iron is first deposited and later partially altered to the oxide and hydroxide state without affecting the carrying power of the current passing between the anode and cathode. Further substantiation of this theory may be found in the fact that analyses of the dull iron plate show that iron constitutes only from 95% to 97.5% of the product and that the hardening contaminants are oxide and hydroxide compounds which can be easily removed by annealing in a hydrogen atmosphere.

My improved iron is sufficiently brittle as deposited at the cathode electrodes to permit economical crushing or grinding and contains iron oxides and iron hydroxides together with a small amount of chlorine, totaling approximately 3% to 5% of the deposit. This product has a dark gray color and is herein called "dull iron plate." Other physical characteristics of my dull iron plate are its hardness, diamond scale, ranging from about 400 to 520; and its porosity which gives it a specific gravity ranging from approximately 6.3 to 7.25. By crushing or grinding it may be reduced to particles of the desired size (usually minus 100 mesh) and of equiaxial structure well adapted for use in iron powder metallurgy. Economical grinding to minus 325 mesh size is feasible and advantageous for many uses. The dull iron plate may be ground in a ball mill with air separation, or in any other suitable

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grinder or pulverizer at low cost. It may be pulverized to minus 100 mesh sizes and with 50% or more of the particles of minus 325 mesh sizes in a ball mill at the rate of 20 to 25 pounds per 100 pounds of balls per hour. Ordinary electro-deposited iron of comparable purity pulverizes at a rate of from 0.25 to 1.0 pound per 100 pounds of balls per hour and cannot be pulverized to minus 325 mesh sizes except at prohibitive cost. The hardening impurities, oxides and hydroxides, of my dull iron plate may be reduced and the resulting gaseous elements together with any chlorine carried over from the electrolyte may be driven off by simple annealing treatment leaving a product which is more than 99.5% pure iron. The annealing treatment preferably comprises heating the ground product in a hydrogen atmosphere at approximately 800 degrees C. for from one to three hours, depending on the fineness of the product. Such annealing treatment causes substantial fritting which, in the case of particles in the smaller ranges of sizes forms clusters adapted to withstand the subsequent pulverizing and screening. After the second pulverizing and screening a controlled percentage as high as 85% of the final pure iron powder may comprise particles between 325 and 100 mesh sizes, a large proportion of particles thereof being porous clusters of smaller particles of substantially equiaxial, as distinguished from flat, shapes.

Analyses of a number of specimens of my dull iron plate show the following ranges of composition in percentages by weight:

| | Per cent. |
|--|-----------|
| Total cathode iron | 95-97.5 |
| Cathode chlorine | .3-.6 |
| Weight loss after heating in nitrogen at 950 degrees C. for one hour | 1.00-1.55 |
| Weight loss after heating in hydrogen at 950 degrees C. for one hour | 2.00-3.55 |
| Total iron after reduction | 99.5-99.9 |

By the annealing treatment in a hydrogen atmosphere, without previous heating in a nitrogen atmosphere, the weight loss amounts to from 3 to 5% by weight.

Typical examples of the physical structure of powders produced from such dull iron plate are as follows:

Example 1

The dull iron plate was ground in a ball mill with air separation to produce a powder all of which passed through a screen having 100 openings per lineal inch and 75% of which, by weight, passed through a screen of 325 mesh size. This powder was then annealed in a hydrogen atmosphere and maintained at a temperature of approximately 800 degrees C. for one and one-half hour. The resulting fritted mass, after cooling, was pulverized in a hammer mill in closed circuit with a screen of 100 mesh size. Numerous tests of the final powder showed the following physical properties:

Flow rate, 50 grams through Hall flow meter, 30 to 33 seconds
Screen analyses:
All minus 100 mesh
70% plus 325 mesh
30% minus 325 mesh
Apparent density: 2.40 to 2.45 grams per cc.
Apparent density variation: .05 gram per cc.

Example 2

Initial ball mill powder screen sizes, same as Example 1

Annealing treatment: Same as Example 1
Screen analysis of final powder (after second grinding):

All minus 80 mesh
80% plus 325 mesh
20% minus 325 mesh

Flow rate: 34 to 36 seconds

Apparent density: 2.15 to 2.20 grams per cc.

Apparent density variation: .05 gram per cc.

Example 3

Initial ball mill powder screen sizes:

All minus 100 mesh
50% minus 325 mesh
50% plus 325 mesh

Annealing treatment: Same as Examples 1 and 2
Screen analyses of final powder:

All minus 80 mesh
80% plus 325 mesh
20% minus 325 mesh

Flow rate: 30 to 32 seconds

Apparent density: 2.65 to 2.70 grams per cc.

Apparent density variation: .05 gram per cc.

All tests show that the finished product flows readily and has remarkably uniform apparent density, since the apparent density variation for each example amounted to only .05 gram per cc. Moreover, the finished powders have unusually uniform screen size distribution. Microscopic examination shows further that the marked increase in grain sizes above 325 mesh in the final product as compared with the product of the first grinding treatment is due to the fritting of the finer particles in clusters under the annealing temperature so that clusters of highly porous and substantially equiaxial structure form a major fraction of the finished powder. Uniformity of apparent density is of great importance since it is a major factor in imparting a uniform compression ratio to the powder thereby greatly facilitating the cold compacting operations. Since the second grinding does not reduce a large proportion of the original particles to original size and form, the particles are not reworked and hardened as in the case of ordinary iron powders formed from bright iron plate. Consequently my final powder is softer and more amenable to compact pressures. Its good flow property further facilitates the filling of intricate die cavities and promotes uniformly reliable results.

According to the present commercial practice in cold die pressing operations, pressures within the range 30 to 100 tons per square inch are employed and my improved powder shows substantially no tendency to increase in volume when such pressures are released from the compacted articles. The green or unsintered strength of the compacted articles or bodies formed from my powder are sufficiently high so that the articles may be handled and transferred from the cold dies to the sintering ovens readily and without danger of breakage. Further, according to present commercial practice, green compacts are subjected to sintering temperatures of the order of magnitude of 1000 to 1100 degrees C. for periods of from one to three hours, depending on the size of the compact. Articles so sintered and comprising my improved powders show less than

0.5% shrinkage due to the sintering treatment and my tests indicate that the shrinkage usually ranges from .05 to .40%. The several advantageous properties described result in finished articles which are so accurately formed to dimension that machining is seldom required even for precision products.

Test bars comprising the powders of Examples 1, 2 and 3, hereinbefore described, formed under 30 tons per square inch pressure and sintered for one and one-half hours at 850 degrees C. have tensile strength ranging from 23,000 to 26,000 pounds per square inch and show elongation under test equal to from 7% to 10% in one inch. Improved compaction as well as unusually equiaxial grain structure and lack of planes of weakness are evident from microscopic examination of polished surfaces of the compacts. The pure iron powder may be mixed with other substances to modify the properties of the end product.

Having described my invention, what I claim as new and desire to protect by Letters Patent is:

1. An electrolytically deposited, porous iron characterized by its dull gray color, hardness, diamond scale, 400 to 520; specific gravity between 6.3 and 7.25; weight loss after heating in nitrogen at 950 degrees C. for one hour, 1.00 to 1.55%; weight loss after heating in hydrogen at 950 degrees C. for one hour, 2.00 to 3.55% and total iron after reduction, above 99.5%.

2. An iron powder characterized by its dull gray color, specific gravity between 6.3 and 7.25; weight loss after heating in hydrogen at 950 degrees C. for one hour, 3.0 to 5.0%, all particles being of 80 mesh and smaller sizes and a major fraction of the particles by weight being of minus 325 mesh sizes and of substantially equiaxed shape.

3. An electrolytically deposited iron characterized by its specific gravity between 6.3 and 7.25; hardness, diamond scale, 400 to 520; the hardening impurities comprising oxide and hydroxide compounds which are readily removable by annealing, and the purity after reduction being above 99.5%.

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