Nov. 25, 1930. R. D. PIKE 1,782,909

APPARATUS FOR THE ELECTRODEPOSITION OF IRON

Filed July 20, 1926 3 Sheets-Sheet 1

Fig. 1.

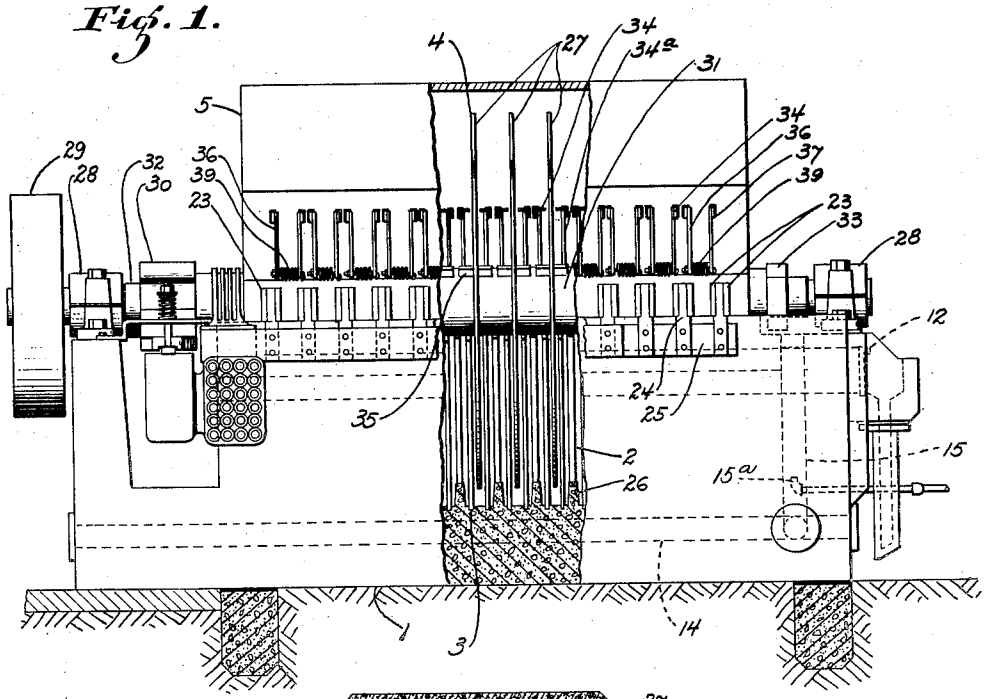
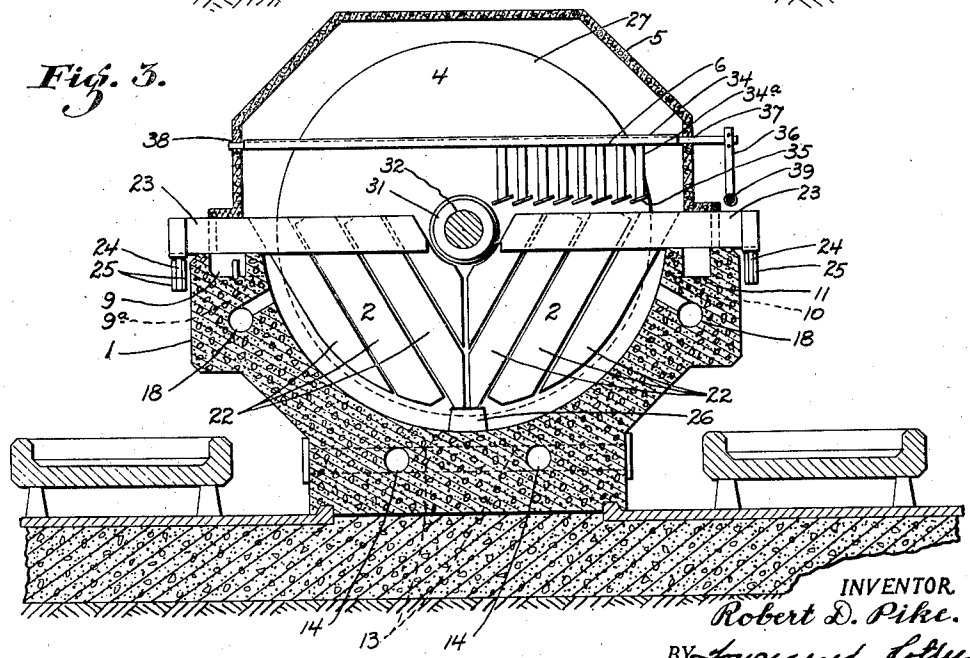


Fig. 3.



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APPARATUS FOR THE ELECTRODEPOSITION OF IRON

Filed July 20, 1926 3 Sheets-Sheet 2

Fig. 2.

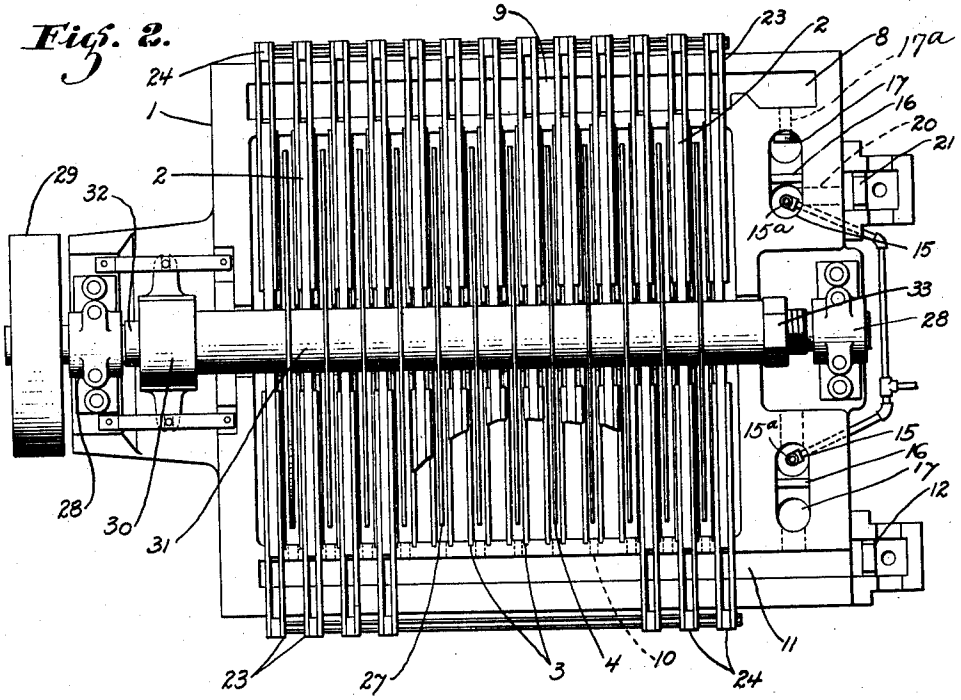
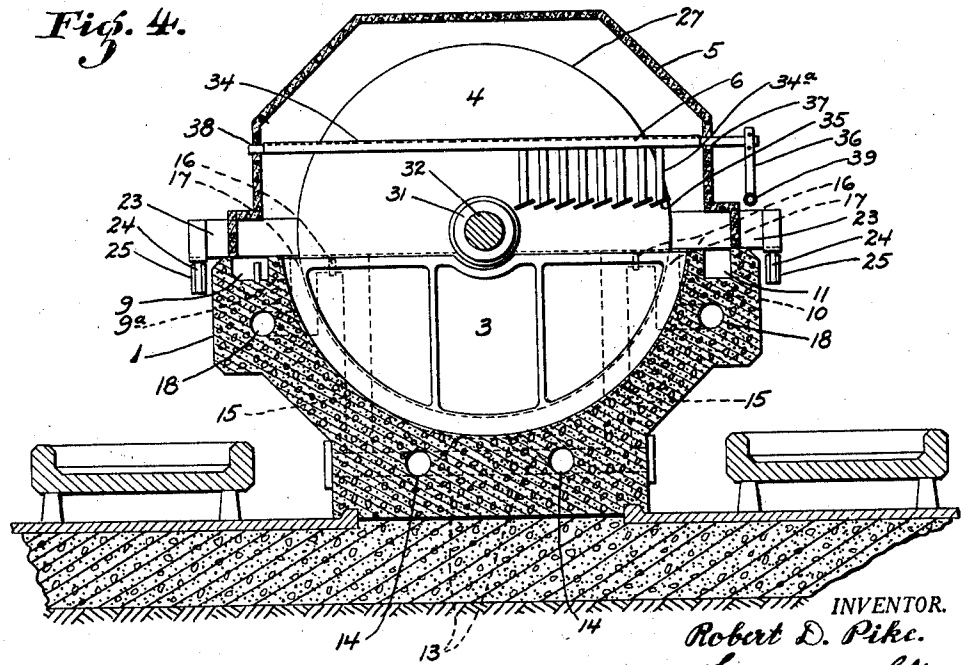


Fig. 4.



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APPARATUS FOR THE ELECTRODEPOSITION OF IRON

Filed July 20, 1926 3 Sheets-Sheet 3

Fig. 5.

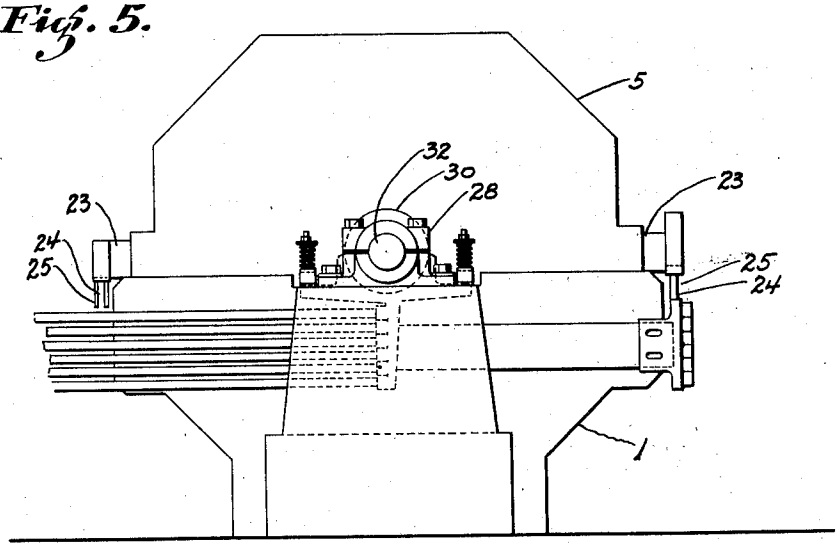
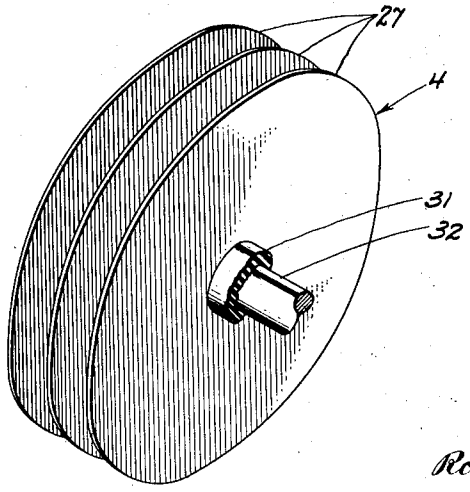


Fig. 6.



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Patented Nov. 25, 1930 1,782,909

UNITED STATES PATENT OFFICE

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APPARATUS FOR THE ELECTRODEPOSITION OF IRON

Application filed July 20, 1926. Serial No. 123,626.

This invention relates to an improved method of electro-deposition of iron. It has particular reference to an improvement in deposition of iron from solutions in electrolytic cells with insoluble anodes, but certain features of my invention are also applicable to deposition of iron in cells with soluble iron anodes.

Up to the present time no commercially successful method has been devised for deposition of iron in electrolytic cells with insoluble anodes; nor have means hitherto been known for making thick deposits of ¼ inch or more of substantially homogeneous electrolytic iron with a relatively smooth surface at current densities much in excess of 15 amperes per square foot, whether in cells with insoluble or soluble anodes.

In prior known methods for making plates of electrolytic iron from solutions in cells with insoluble anodes, hydrogen deposition on the cathode causes the growth of trees or snags of iron which pierce the diaphragms, causing their destruction when the cathode is lifted from the cell. This renders the method impractical because of the high cost of the diaphragms and the interruption to operation.

I have discovered that, if iron be deposited upon a slowly moving cathode surface part of which surface is continually exposed to the atmosphere, an effect is produced which is beneficial to the deposit, and is apparently the result of a depolarizing reaction whereby the oxygen of the atmosphere combines with a portion of the cathodically deposited hydrogen, or with the hydrogen ions in the layer of solution which adheres to the surface of the deposit, thereby inhibiting the otherwise bad effect of hydrogen upon the physical nature of the deposit.

The action of the atmospheric oxygen also tends to produce basic salts which, in time, tend to give the deposit an oxidized appearance, but I have discovered that by employing a rubber brush or wiper, which continually rubs on the exposed deposit with a gentle pressure, the basic particles are removed and the deposition of iron in the form of a substantially smooth, homogeneous, fully metallic deposit, free from trees or snags, can be continued for much longer periods of time and with higher current densities, resulting in greater thicknesses of the deposit, than is possible by present known methods. It is also likely that the rubber brush, or wiper, has the further beneficial effect of smoothing out inequalities of hydrogen ion concentration in the thin layer of catholyte solution which adheres to the deposit as it emerges from the solution in the cell, and that this, in turn, promotes the smoothness of deposits by eliminating differences of hydrogen concentration in adjoining areas of the metal. The wiper also serves to remove minute bubbles of hydrogen. I have discovered that if the surface of the rotating deposit be rubbed with soft iron strips applied under gentle pressure, an even better result is attained than with rubber, because the latter tends to contaminate the deposit to some extent with C and S, while no contamination results from the use of soft pure iron strips. In using the pure iron strips I find the best position for placing them is on the down-moving side of the deposit, just before it re-enters the catholyte. I have also found that if, for example, the total period of deposition is from two to three weeks, it is not necessary to apply the strips for more than the first two or three days. This is probably explained by the fact that the strips promote the formation of uniformly sized grains in the young deposit, and uniformly sized grains, once having been formed, tend to continue to grow as more or less uniformly sized grains, during the entire period of deposition. This is in accordance with a well-recognized law of grain growth in metals, which is to the effect that if the grains are of uniform size to start with, they tend to remain uniform in size during growth; but if the mass is made up of large and small grains, the former tend to grow even larger at the expense of the latter.

I consider the rubbing of the deposit with soft strips of pure iron, as just described, to be the preferable method for applying my invention, and by its use I have produced iron plates about ¼ inch thick and composed entirely of homogeneous, non-porous iron. Samples

of such iron after annealing, when prepared with polished and etched surfaces and examined in the metallograph at 1,000 diameters, show a pure structure of ferrite grains with no inclusions of oxide and no porosity. Furthermore, these plates can, after one annealing for a few minutes at 1,000 degrees centigrade, be cold-rolled into thin sheets without any work hardening. It has not been possible by hitherto known commercial methods to produce directly flat cathode plates of electrolytic iron having the above properties. It is well known that thin cylinders of electrolytic iron of good physical properties have been produced on fully-submerged, rapidly rotating cylinders by the so-called Grenoble process of Societé Le Fer; but it is entirely impractical to construct such cells for cheap production of iron from solutions with insoluble anodes, because of mechanical difficulties, but principally because of the high investment cost per unit output in unit time. My present invention is the first known method for producing large quantities of the highest grade of electrolytic iron by a cheap process comparable in costs to well known electro-metallurgical processes for producing zinc and copper; and it is the only successful method worked out, up to the present time, for producing electrolytic iron from solutions in diaphragm cells with insoluble anodes. When this process is carried out in connection with the process covered by my pending application for metallurgical process, Serial Number 87,509, I am able to produce iron which is more pure than is possible by any soluble anode process, including the above-mentioned Grenoble process. This follows because practice has demonstrated that certain impurities, such as sulphur and phosphorus, tend to pass from the anode to the cathode, and if the former is insoluble and the solution properly purified, this source of contamination is removed.

My method eliminates the growth of trees or snags on the deposit and prevents injury to the diaphragms in cells with insoluble anodes.

This latter feature is of essential importance because of the high cost of pure asbestos diaphragms, which latter material alone will resist the attack of ferric chloride.

If deposition is made at 35 to 50 amperes per square foot of submerged cathode area, the same can be continued for as long as three weeks, and deposits can be made ¼ inch or more in thickness, having relatively smooth surfaces of deposition and a structure consisting entirely, after one annealing at 900° to 1000° centigrade, of pure ferrite grains free from nonmetallic inclusions, a result not attainable by any other known process. The thick electrolytic iron produced by this process is so non-porous and free from inclusions of oxide and electrolyte as to be on this account a novel and valuable product, particularly as a new material for the manufacture of high-grade magnetic materials.

When the period of deposition is finished it is usual to strip the deposited iron from the cathode basis metal, which is preferably that of the cathode disc, or it may be a cylinder; but the disc method is the preferable way for carrying out my process. One way to do this is to electrolytically deposit upon the discs in a suitable cell for that purpose, and before they are inserted in the iron cells, about .001 inch of electrolytic lead. The iron is then deposited upon the lead surface. When the deposition has been completed, the discs are heated to a temperature a little above the melting point of lead. This of course melts the lead and effects an easy separation of the electrolytic iron from the basis metal. The discs are then cleaned, usually with a sand blast, coated again with lead, and put back in the iron cell.

A preferable method for stripping is to cover the starting disc with a coating of blue oxide. This is done by mounting the discs on a mandrel and slowly rotating in a furnace which is brought up to a temperature of about 1000 degrees centigrade. The discs are then cooled in a current of air and passed through flattening rolls to make substantially flat. They are then pickled for a few minutes as anode in an electrolytic bath of dilute hydrochloric acid, care being taken not to entirely remove the coating of oxide. A surface thus prepared is in condition to take and securely hold a deposit of iron while the same is being electro-deposited, but the entire deposit can be easily removed by a few well directed blows of a hammer.

Having stated the general nature of my invention, I will now set forth, for descriptive purposes but not for limitation, an example of the carrying out of the method in practice. The nature of my discovery is of broad application, and applies to any type of apparatus in which the necessary conditions—(1) of continual exposure of a portion of the moving deposit to the atmosphere; and (2) the rubbing or wiping of the deposit with a device of suitable nature, preferably soft iron—are met. It will be understood that an improvement in deposition is effected by condition (1) alone, and that by further applying condition (2), deposition can be made thicker and the physical nature of the deposit is further improved.

In the drawings:

Figure 1 is a part longitudinal section, part elevation, of a 12-cathode 60-inch cell.

Figure 2 is a plan view of same with cover removed.

Fig. 3 is a section through an anode compartment showing the anode.

Figure 4 is a section through the anode compartment showing the diaphragm.

Figure 5 is an end elevation showing the electrical connections to the commutator.

Figure 6 is a view of one of the cathode discs.

The cell illustrated is a commercial unit having twelve 60-inch cathode discs and producing 331 pounds of iron daily at a cathodic current density of 35 amperes per square foot and a cathodic current efficiency of 95%. The cell voltage is 3.48 and the D. C. power required is 1.65 kilowatt hours per pound of Fe. The cell assembly comprises the following principal parts: The reinforced concrete tank 1, which is preferably made of reinforced Portland cement concrete which has been dipped in molten sulphur to render the concrete immune to attack by ferrous and ferric chloride; the graphite anodes 2 (I have found that the life of these anodes is greatly increased by dipping them in molten sulphur, and at the same the electrical resistance is increased but little); the asbestos cloth diaphragms 3, which are described in my co-pending application, Serial Number 58,010; the cathode disc assembly 4; the cover 5; the rubber assembly 6.

Incoming electrolyte, consisting principally of a water solution of ferrous chloride containing about 12% Fe^{xx} and .05% or less Fe^{xxx} with pH about 2.5 and at a temperature of 80° centigrade to 90° centigrade, enters the cell at 8, and flowing through the distributing channel 9, enters into each cathode compartment through side branches 9^a. About twice as much electrolyte is introduced as is actually required, the surplus passing through branches 10 into channel 11 and thence out of the cell over wier 12, which is employed to keep the level constant in the cathode compartments. Catholyte flows through the porous diaphragms 3 into the anode compartments, and thence through the channels 13, of which there are two in the bottom of each anode compartment, into the longitudinal passages 14, which connect with the upcoming channels 15. In these latter are placed steam ejectors 15^a which cause an upward flow of anolyte in the channels 15 and discharge same over dams 16 into channels 17, which connect by branches (not shown) with longitudinal channels 18, which in turn connect by side branches with each anode compartment. This arrangement provides an active circulation of anolyte downwardly in the anode compartments, which is the proper direction of circulation, because I have found that the ferric chloride as formed at the anode, tends to flow downwardly. A single side channel 20 connects with a regulatable wier 21, by means of which the draw-off of anolyte from the cell is regulated. As the porous diaphragms become blinded it is desirable to by-pass fresh electrolyte through a suitable valve 17^a (Fig. 2), directly from 8 into 17 so as to control the percentage of Fe^{xxx} in the anolyte. Ordinarily the anolyte will contain 10% total Fe, of which 4.5% to 5% is Fe^{xxx}, and the Fe^{xxx} content of the catholyte will not be above .05%. The rate of circulation of anolyte through the anode compartments is many times the rate of withdrawal of anolyte over wier 21. The exact amount of circulation will be decided by the amount of steam required in the steam ejectors to maintain a temperature of 90 degrees centigrade to 95 degrees centigrade in the anolyte.

The anodes, 2, consist of anode plates 22 secured to anode cross-bars 23, which in turn engage copper fingers 24 which are in electrical contact with the positive bus bars 25. The anodes are supported at their lower extremities by piers 26.

The diaphragms 3 are set into grooves (not shown) provided in the cell body, and are cemented into place with suitable mortar.

The cathode disc assembly 4 is described in my copending application, Serial Number 58,010, and is comprised of discs 27, journal and bearings 28, pulley 29, negative commutator 30, protective rubber sleeves 31, the shaft 32, and keeper nut 33. The shaft assembly is rotated at from one to two R. P. M. by suitable driving means (not shown).

I have found that satisfactory deposition of iron cannot be carried out if the rotating discs are completely exposed to the chilling effect of the atmosphere. If so exposed the deposit cracks and peels away from the basis metal. On this account the hood 5 is provided. This is made of a suitable rubber-covered steel supporting frame (not shown). The hood proper is preferably made of asbestos lumber, and is thermally insulated by a layer of cork-board on the outside. Suitable sight holes (not shown) are provided, and a vent (not shown) is provided for removing steam from beneath the hood and conducting the same away from the cell room. The entire hood is removable by lifting, and is of course taken off the cell when the disc assembly is being placed or the deposits removed.

Rubber assembly 6 comprises supporting rod 34, which is preferably made of steel, rubber-covered. Depending from 34 and securely fastened thereto are rubber-covered flat steep springs 34^a, to the lower end of which are securely attached the soft iron strips 35. Supporting member 34 is removably held in the hood at 37 and 38 by supports the details of which are not shown. An arm 36 is attached to the outer end of member 34. A spring 39 is employed to draw together the arms 36 of the two rods 34 situated on opposite sides of each cathode, thus causing the rubbers 35 to press with a gentle pressure upon the faces of the deposit.

In operation, after a fresh cathode assembly has been placed, the cover is put on the

cell and the rubber assembly inserted. The current is gradually brought up to full strength of 35 amperes per square foot of submerged cathode area in eight hours. About two hours after starting the current the pressure is applied to the brushes. After two to three days the rubber assemblies are removed, and deposition is continued for from ten to twelve days more. After a run the assembly will hold about 5,000 pounds of new electrolytic iron. The discs are removed from the assembly and the new iron recovered as complete discs by a few well directed blows of a hammer.

As is well known to electro-metallurgists, each metal has certain characteristic peculiarities involving difficulties which have to be overcome in electro-deposition. Iron is a very difficult metal to successfully deposit, and the merit of my process resides in overcoming certain specific obstacles in the way of large scale deposition of pure homogeneous deposits of iron, which obstacles have not been hitherto overcome.

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

1. A cell for electrolytic deposition of iron comprising a plurality of alternating anode and cathode compartments separated from each other by porous diaphragms, insoluble anodes suspended in the anode compartments, rotating disc cathodes mounted on a shaft and dipping into the electrolyte in the cathode compartments, the upper part of said disc being above the level of the electrolyte, means for introducing fresh electrolyte into the cathode compartment, and an overflow wier for keeping a substantially constant level of catholyte, means for causing a downward circulation of anolyte in the anode compartment, means for heating the anolyte during such circulation, and means for withdrawing the net flow of anolyte from the cell and maintaining its level slightly below that of the catholyte.

2. A cell for electrolytic deposition of iron comprising a plurality of alternating anode and cathode comparements separated from each other by porous diaphragms, insoluble anodes suspended in the anode compartments, rotating disc cathodes mounted on a shaft and dipping into the electrolyte in the cathode compartments, the upper part of said disc being above the level of the electrolyte, means for introducing fresh electrolyte into the cathode compartment, and an overflow wier for keeping a substantially constant level of catholyte, means for causing a downward circulation of anolyte in the anode compartment, means for heating the anolyte during such circulation, means for withdrawing the net flow of anolyte from the cell and maintaining its level slightly below that of the catholyte, and a thermally insulated hood for covering the exposed part of the assembly of cathode discs to prevent cooling by the outside atmosphere.

3. In a cell for electrolytic deposition of iron in combination with partially submerged rotating cathode discs, rotatably mounted rods on each side of the separate discs, spring strips attached to and depending from the rods facing the downwardly rotating faces of the discs, soft iron strips attached to the lower end of the spring strips and adapted to engage with their inner edges substantially the entire downwardly rotating faces of the discs, arms attached to one end of each rod and a spring engaging each pair of arms associated with each disc and adapted to cause a pressure of the said iron strips against the faces of the discs.

4. A cell for electrolytic deposition of iron, comprising a plurality of alternating anode and cathode compartments separated from each other by porous diaphragms, insoluble anodes in the anode compartments, rotating disc cathodes mounted on a shaft and dipping into the electrolyte in the cathode compartments, the upper part of said discs being above the level of the electrolyte, means for introducing fresh electrolyte into the cathode compartment, and for maintaining its level substantially constant, means for causing a circulation of anolyte in the anode compartment, means for heating the anolyte during such circulation, and means in communication with the anode compartments for withdrawing the net flow of anolyte from the cell.

5. A cell for the electro-deposition of metals comprising a plurality of alternating anode and cathode compartments separated from each other by porous diaphragms, insoluble anodes in the anode compartments, cathodes in the cathode compartments, means for introducing fresh electrolyte to the cathode compartments and for maintaining its level substantially constant, means for circulating electrolyte and for controlling its temperature during circulation, means for maintaining the level of the anolyte substantially constant, and slightly below the level of the catholyte, and means for withdrawing the net flow of anolyte from the cell.

ROBERT D. PIKE.