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ELECTROLYTIC PROCESS OF PRODUCING DUCTILE IRON

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My invention relates to the electrodeposition of iron in ductile form. By this is meant iron which can be bent, rolled or drawn within reasonable limits just as it leaves the bath of electrolyte and without prior annealing.

An object of the invention is to provide iron which can be rolled or drawn to reduced section, built up to the original thickness by further electrodeposition of ductile iron and again rolled or drawn, with repetition of these cycles of deposition and working as required in order to produce sheets, wire, tubes, etc., as set forth in a copending application, Serial Number 214,194, filed August 19, 1927.

Another object of the invention is to provide an electrolytic having but few variables which influence the ductility quality, these variables being subject to ready measurement and control, so that on long continued use of the electrolyte, as is necessary in commercial operations, the changes which inevitably occur in any such electrolytic method can be compensated for in a simple manner by relatively unskilled labor, and thus the continued deposition of ductile iron of constant physical qualities attained.

Another object of the invention is to prevent the accumulation in the electrolyte of sediments due to basic iron salts which tend to give rough deposits, and which also tend to clog the filter where one is used for clarifying the electrolyte.

Another object is to provide for an even and quantitative solution of the anodes without the formation of coatings of hydroxides of iron or basic salts on the active anode faces. Such coatings greatly reduce the current efficiency and also slow down the attacking of the anodes.

Another object is to provide an electrolytic method permitting close spacing of pairs of anodes and cathodes, thus reducing the voltage drop through the electrolyte and lowering the cost of the electrical energy necessary for making iron.

Another object is to provide for such movement of the electrolyte as will insure an even deposit at the cathode without, however, agitating in such a way as to cause harmful changes in the state of valence of the iron in the electrolyte (as by oxidation). Many processes, I find, agitate or circulate the electrolyte in such uneven or irregular fashion that local changes brought about at the cathode face cause corresponding irregularities in the iron deposited there.

Another object of the invention is to provide means for controlling the addition of reagents intended for maintaining the necessary acidity of the electrolyte as herein set forth.

These and other objects of my invention which will be pointed out hereinafter or will be apparent to one skilled in the art upon reading these specifications, I accomplish in that certain process which I shall now more particularly describe.

The basis of my invention is that, other electrolytic conditions being appropriate, iron can be electrodeposited in ductile form from a hot ferrous chloride electrolyte by keeping the hydrogen ion concentration of the electrolyte (usually written pH) within the limits 1.5 to 2.5. The pH figure can go to 1.0 or even less without destroying ductility, but there is then a tendency for the current efficiency (weight of iron deposited per ampere hour) to decrease. Also, the pH figure can be somewhat higher than 2.5, but at pH 3.0 the ductility is negligible.

This method of making ductile iron succeeds best with gray cast iron anodes. Steel or commercially pure iron anodes can also be used. Iron sulphide anodes, such as described in my pending application, Serial Number 173,793, cannot be used, for they will not produce ductile deposits under the conditions described herein.

This method however, will not give ductile iron in a ferrous sulphate electrolyte, nor in a chloride electrolyte containing any appreciable amount of sulphate. Why this is so is not evident at this time; but I have established the fact by a careful set of experiments. The method will not give ductile iron at room temperature, nor in fact at any temperature range much short of what is herein specified. The reasons for

this have not been investigated; but experiments have given this result.

In carrying out my invention I prepare an electrolyte of ferrous chloride which is very concentrated in iron; a convenient strength is 80% saturated at room temperature. The pH of this is then adjusted by the addition of hydrochloric acid until it comes within the range 1.5 to 2.5; a convenient pH is 2.0. The adjustment is effected with the aid of color indicators, or by electrometric pH measurements such as are now well known. The electrolyte is placed in the electrolytic tank which is provided with means for maintaining the temperature at 95 to 100° C.—the preferred working range for this method. There may also be provided a pump for circulating the electrolyte, inlets and outlets for the electrolyte designed to secure regular and uniform circulation between anodes and cathodes, and a filter through which the electrolyte is passed, the clarified electrolyte being returned to the electrolytic tank continuously. I have used a sand filter and a rotary pump with success for this work.

Into the electrolyte are set pairs of anodes and cathodes of a size and spacing appropriate to the size of the tank and the scale of the operation. Nothing in the nature of this invention is apparent that would limit the number of electrode pairs or their size. The spacing can be quite close, since there are practically no sediments in the electrolyte nor on the anode faces, which would tend to cause short-circuiting. Such close spacing permits me to realize the practical advantage of a smaller voltage drop between electrodes. What has been said relates to the "series" system of arranging electrodes for the electrodeposition of metals. Like advantages apply to the "multiple" system.

For anodes, as heretofore stated, gray cast iron, steel or commercially pure forms of iron may be used. A particular advantage has been found inherent in the use of gray cast iron, other than its cheapness. Anodes of this material when used under the electrolytic conditions herein described evolve numerous small gas bubbles which are shot off with considerable velocity normal to the anode face. This liberation of gas takes place uniformly all over the anode face and the result is a very thorough and uniform agitation of the electrolyte such as is important for the formation of smooth and even deposits. I have not observed this phenomenon to any like degree when using other kinds of iron or iron-containing anodes. The graphitic carbon or other insoluble substance associated with the gray cast iron attach themselves as a tough, adherent coating to the anode face as it dissolves electrolytically. This coating neither increases appreciably the resistance of the electrolytic path nor tends to loosen and float off into the electrolyte; nor does it tend to migrate because of electrolytic effects. Hence, there are no deleterious results from its presence. After a certain length of time it is desirable to replace the anodes with clean ones while the accumulated coating is removed by iron brushes or otherwise so that the cleaned anodes may be put back again. In my method of electrodepositing ductile iron no porous cups, diaphragms or bags are necessary to separate anodes or cathodes. They may be used if desired in case any particular advantage seems to be gained; but I have found that smooth, even and uniform ductile deposits of iron can be made without them and their omission saves expense in labor and maintenance and also saves the electrical energy which is necessary because of increased voltage drop when such appliances are used.

Having the electrolytic tank filled with electrolyte at 95 to 100° C., the pump and filter connected in, and the anode and cathode pairs connected to a plating generator with voltage and amperage appropriate for the desired rate of making iron and the system of electrical connections for anodes and cathodes, I proceed to operate my bath at a cathode current density of 50 to 150 amperes per square foot, or more, the rate of circulation of electrolyte by the pump being adjusted in accordance with the current density as shown best by experience. One hundred amperes per square foot has been found a convenient current density in most of my work. Current density has not been found a fundamental factor in producing ductile iron by my method, inasmuch as a satisfactory degree of ductility can be obtained with a wide variation in current density.

After iron has deposited for a while a pH test will show that the pH has increased—in other words, some of the free acid in the electrolyte has been consumed. If the test shows that the pH is much removed from 2.0, the figure herein set as a desirable means, enough dilute hydrochloric acid is added (as determined by outside test on a portion of the electrolyte) to bring the main body of the electrolyte back to the pH desired. Such tests and adjustments are made as often as experience shows necessary and once a routine is worked out for a given set of operating conditions, viz., current density, current in relation to volume of electrolyte and rate of circulation, the procedure is standardized for any number of repetitions of the same set of conditions.

A more satisfactory way to keep the pH adjustment is by means of an outfit for determining pH values continuously and automatically. This is used in conjunction

with a reservoir of dilute hydrochloric acid from which acid is admitted to the electrolyte by a valve controlled by the electrolytic pH indicator. Such an apparatus lends itself readily to this operation and eliminates all necessity for hand control or for an operator to determine pH values. Apparatus of this kind is now standardized and in commercial use for many operations of this nature and hence need not be described here.

The hydrochloric acid for restoring the pH of the electrolyte can of course be made by electrolytic or chemical or electrochemical processes constituting, if desired, a part of the chain of manufacturing operations leading to electrolytic iron. In many cases this reduces the cost of the acid. Details of process for the regeneration of acid are not necessary to the understanding of my present invention. I have used two such methods: (1) Formation of ferric chloride at the anode from a portion of the electrolyte by the use of an anode diaphragm, and subsequent reduction thereof to ferrous chloride by means of nascent hydrogen, with formation of an equivalent amount of hydrochloric acid, thus: $2FeCl_3+H_2=2FeCl_2+2HCl$. (2) Formation of ferric chloride as in (1), then reduction of this by means of sulphur dioxide to form ferrous chloride and equivalent hydrochloric acid. The sulphuric acid formed during this operation is removed by precipitation with barium chloride and filtration. In both methods the ferrous chloride plus the hydrochloric acid formed is added to the electrolyte as needed, either by hand or automatically as described.

Various modifications may be made in my invention without departing from the spirit of it.

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

1. An electrolyte process for the production of ductile iron which comprises electroplating iron on a cathode, from an anode comprising free iron, through an electrolyte of ferrous chloride rich in iron, and maintaining the hydrogen ion concentration of said electrolyte between 1.5 and 2.5 pH value by additions of hydrochloric acid as required during continuous electrolysis, the acid electrolyte being maintained at a temperature between 95° and 100° C.

2. An electrolyte process for the production of ductile iron which comprises electroplating iron on a cathode, from an anode comprising free iron, through an electrolyte of ferrous chloride rich in iron, and maintaining the hydrogen ion concentration of said electrolyte between 1.5 and 2.5 pH value during continuous electrolysis, the said electrolyte being maintained at a temperature between 95° and 100° C., and continuously circulating and filtering said electrolyte.

3. A process for the electrolytic production of ductile iron which comprises using an iron anode, and a ferrous chloride electrolyte substantially free from sulphates and maintained at a temperature between 95° and 100° C., and adding to the said electrolyte, during the electrodeposition, acid to maintain the acidity thereof at approximately 2.0 pH and maintaining the ferrous character of said electrolyte.

4. A process for the electrolytic production of ductile iron which comprises using an iron anode, and a ferrous chloride electrolyte substantially free from sulphates and maintained at a temperature between 95° and 100° C., and adding to the said electrolyte, during the electrodeposition, acid to maintain the acidity thereof to approximately 2.0 pH, the said electrodeposition being carried on at a current density greater than 50 amperes per square foot.

5. A process for the electrolytic production of ductile iron which comprises using an iron anode, and a ferrous chloride electrolyte substantially free from sulphates and maintained at a temperature between 95° and 100° C., and adding to the said electrolyte, during the electrodeposition, acid to maintain the acidity thereof at approximately 2.0 pH, the said electrodeposition being carried on at a current density greater than 50 amperes per square foot, and continuously circulating and filtering the said electrolyte.

6. A process for the electrodeposition of iron comprising the use of an anode of cast iron, a cathode to receive the deposit, an electrolyte of ferrous chloride approximately 80% saturated at a pH between 1.5 and 2.5, and a plating current density around 100 amperes per square foot, while maintaining the said electrolyte at a temperature of between 95° and 100° C., and at the said acidity by the addition as required of hydrochloric acid.

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