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Index at acceptance 70C4 [LVIII (5)].

PROVISIONAL SPECIFICATION.

IMPROVEMENTS IN OR RELATING TO THE ELECTROCHEMICAL PRODUCTION OF IRON POWDER
FROM MILL SCALE PRODUCED DURING ROLLING OPERATIONS IN STEEL ROLLING
MILLS OR MATERIALS OF SIMILAR NATURE.

COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH RAFI MARG, NEW DELHI-1, INDIA, AN INDIAN
REGISTERED BODY INCORPORATED UNDER THE REGISTRATION OF SOCIETIES ACT (ACT XXI OF 1860).

The following specification describes the nature of the invention.

This is an invention by Handady Venkatakrishna Udapa, Pennagaram Vyasa Rao Vasudeva Rao and Rengaswamy Vijayavalli all scientists of Central Electrochemical Research Institute, Karaikudi-3 and all Indians.

This invention (relates to improvements in or) is relating to production of iron powder from mill scale by direct electrolytic reduction.

Hitherto it has been proposed to produce iron powder from mill scale and the like only by thermal reduction at high temperatures with reducing gasses like Hydrogen or Hydrocarbons or mixture of the same. No electrolytic method has been known to operate for directly reducing mill scale and the like. The known electrolytic methods propose to use aqueous solution of iron compounds. The object of this invention is to produce iron powder by directly reducing mill scale by an electrolytic process which has certain advantages over the hitherto known processes.

To these ends the invention broadly consists in direct electrolytic reduction of the mill scale or the like in solid phase kept on a cathode substrate in alkaline electrolyte. The mill scale is powdered to a mesh size of at least—150 and kept as a sediment at the bottom of a container preferably a metallic one, which itself is used as the cathode. An anode of a metallic wire mesh or perforated sheet or a grid which is not attacked by the alkaline electrolyte is disposed over the bed of the mill scale powder but not touching the same. A 10—50% by wt. solution of an alkali metal hydroxide like hydroxide of potassium, sodium or lithium is used at the electrolyte. A current density of 10—50 A/dm² based on the apparent cathode surface area is applied. The current efficiency for the reduction has been found to be 85% assuming the formula for the mill scale as Fe₃O₄. After the reduction is over, the alkali electrolyte is drained off and stored for reuse; the reduced powder is washed thoroughly till the pH of the wash water is between 6.5 and 7.5 and then stabilised by finally washing with 2 to 3% solution of soap or 0.1 to 1% of potassium dichromate. A heat treatment in a hydrogen atmosphere for about 40-45 minutes at a temperature of 800—950°C is necessary to improve the free metallic content from about 75—80% as obtained in the cell to 92—95% after heat treatment.

The following typical examples are given to illustrate the invention.

EXAMPLE 1

Weight of mill scale taken=5 g.
Concentration of electrolyte used=20%
Current density=5.0A/dm²; Current passed=1A
Duration of electrolysis=4.7 hrs.
Average voltage=2.15 V; Wt. of powder obtained=3.7g.
Purity of powder before heat treatment=74.5% metallic
Purity of powder after heat treatment=93% metallic.

EXAMPLE 2

Weight of mill scale taken=100 g. (—150 mesh size)
Concentration of sodium hydroxide=40%
Current density=20A/dm²; Current passed=20 Amp.
Duration of electrolysis=4.7 hrs.
Average voltage=3.2 V; Wt. of powder obtained=71.5 g.
Metallic content before heat treatment=76.44%
Metallic content after heat treatment=95.43%
Average energy consumption=4 KWH(AC)/Kg.

The following are among the main advantages:

1. The mill scale and the like material need not be brought into solution for electrolytically obtaining iron powder from the same.
2. A large quantity of the mill scale which is otherwise thrown as a waste in sheet rolling & wire & rod drawing and other extrusion operation can be converted to electrolytic iron powder by this very competitive & economic process.
3. The electrolyte can be reused a number of times (at least 10 cycles) with only a small loss during handling. Energy costs are comparable with the conventional electro-deposition process. Since most other unit processes are not involved, the process is more economical than conventional electrolytic process.
4. The process lends itself for ready scaling up, so that high amperage cells can be easily employed for the process.

R. BHASKAR PAI,
PATENTS OFFICER,

Council of Scientific and Industrial Research.

Dated this 3rd day of March 1970.

COMPLETE SPECIFICATION

IMPROVEMENTS IN OR RELATING TO THE ELECTROCHEMICAL REDUCTION OF IRON POWDER FROM MILL SCALE PRODUCED DURING ROLLING OPERATIONS IN STEEL ROLLING MILLS OR MATERIALS OF SIMILAR NATURE.

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH, RAJI MARG, NEW DELHI-1, INDIA, AN INDIAN REGISTERED BODY INCORPORATED UNDER THE REGISTRATION OF SOCIETIES ACT (ACT XXI OF 1860).

The following specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed.

This is an invention by HANDADY VENKATAKRISHNA UDUPA, PENNAGARAM VYASA RAO VASUDEVA RAO and RENGASWAMY VIJAYAVALLI, all of the Central Electro-chemical Research Institute, Karaikudi-3, all Indian citizens.

This invention relates to improvements in or relating to the electrochemical production of iron powder from mill scale produced during rolling operations in steel rolling mills or materials of similar nature.

Hitherto it has been proposed to produce iron powder from mill scale and the like only by thermal reduction at high temperatures with reducing gases like hydrogen or hydrocarbons or mixture of the same. No electrolytic method has been known to operate for directly reducing mill scale and the like. The known electrolytic methods propose to use aqueous solution of iron compounds.

In the hitherto known processes, only iron compounds in aqueous solution have been used to deposit iron powder by conventional electrolytic method. This involves bringing the iron compound into solution and other subsequent unit operations such as filtration. Further it is also very cumbersome to get the mill scale into such a solution. These drawbacks are obviated by the present process of direct reduction in which the mill scale need not be brought into solution and iron powder is obtained by direct electrolytic reduction of the mill scale in the solid phase.

The object of the invention is to utilise mill scale which is available in large quantities as a byproduct from steel rolling industries.

Iron powder of any desired particle size is obtained by the direct electrolytic reduction of byproduct mill scale, the reduction being carried out in the solid phase in an electrolyte of an alkali hydroxide. The mill scale is kept as a sediment immersed in the alkaline electrolyte at the bottom of a suitable conducting container and an insoluble anode kept above the sediment, but immersed in the electrolyte. The container itself is used as the cathode and this process of direct reduction offers certain advantages namely (a) this eliminates the intermediate steps of bringing the iron compounds into solution and electrolysis subsequently, (b) avoids handling of large volumes of solutions, (c) the process is simple to operate without involving control of different parameters, (d) the particle size of the end product may be controlled by the particle size of the starting material.

According to the present invention, there is provided a process for the electrochemical production of iron powder from mill scale produced during rolling operations in steel rolling mills or materials of similar nature, the process comprising of direct electrochemical reduction of the scales or materials of similar nature on a metal substrate such as mild steel, copper, stainless steel, nickel or nickel plated mild steel, the container itself being used as the cathode, with an anode of mild steel, nickel plated mild steel, nickel or stainless steel wire mesh parallelly disposed over the bed of the mill scale or materials of similar nature and mounted on a frame so that while immersed in an electrolyte over the

bed of mill scale or materials of similar nature facilitates uniform distribution of current.

The mill scale or materials of similar nature are converted into iron powder by direct electrochemical reduction using an electrolyte of an aqueous solution of sodium, potassium or lithium hydroxide of strength between 5 and 50% (W/V) preferably 40% solution at a current density of 5—50 amp/dm² preferably at 10 amp/dm² and at laboratory temperatures.

The size of the iron powder after reduction is controlled by choosing the same or very near mesh size of the iron oxide scales or materials of similar nature.

The alkali electrolyte is recovered from the cell and reused by making good the loss due to drag out and handling.

The iron powder obtained by direct electrochemical reduction is given a stabilising treatment with 2 to 3% soap solution or 0.1 to 1% potassium dichromate solution.

The iron powder produced by the direct electrochemical reduction process is given a further heat treatment in an atmosphere of hydrogen or dissociated ammonia at a temperature ranging between 750 and 1000°C for a duration varying between 10 minutes and 1 hour.

Thus, iron powder from mill scale and the like obtained from steel rolling industries is produced by the direct reduction of the mill scale and the like kept as a sediment on a cathode wherein the iron powder can be directly produced without bringing the mill scale and the like into solution and subsequent electrolysis of the same. The conversion efficiency is almost 100% and current efficiency ranges between 80 and 90%.

In this process iron powder is produced by direct electrolytic reduction of mill scale and the like in a suitable cell arrangement using an alkaline electrolyte. The cell arrangement consists of a copper, mild steel, stainless steel, nickel or nickel plated mild steel container in which the mill scale and the like is contained in a powder form of suitable mesh size. The container itself is used as the cathode. The anode assembly consists of a mild steel, nickel plated mild steel, nickel or stainless steel mesh suitably disposed over the bed of the powder and mounted on a frame in such a way that, while immersed in an electrolyte of sodium or potassium hydroxide over the bed of mill scale and the same, it will facilitate uniform distribution of current on the cathodic surface. A rectangular mild steel container of dimension 30cm X 25cm was used as cathode in an experiment and nickel plated mild steel was used as anode which was mounted on an insulating frame and disposed 1" over the bed of mill scale of —150 mesh in an electrolyte of 40% NaOH. The current density employed was 10 amp/dm² and 10% excess of the total theoretical current required

to reduce the mill scale taken was passed. At the end the iron powder was discharged from the cell, washed thoroughly till the pH of the wash water is between 6.5 and 7.5 and then stabilised by finally washing with 2-3% soap solution or 0.1 to 1% potassium dichromate solution. A heat treatment in hydrogen atmosphere for about 40-45 minutes at a temperature 800-950°C is necessary to improve the free metallic content from about 75 to 80% as obtained from the cell to 92-99% after heat treatment.

The following typical examples are given to illustrate the invention:

EXAMPLE I

| | |
|---|------------------------|
| Weight of mill scale taken: | 100 g (-150 mesh size) |
| Concentration of sodium hydroxide: | 40% |
| Current density: | 20 amp/dm ² |
| Current passed: | 20 amps |
| Duration of electrolysis: | 4.7 hours |
| Average voltage: | 3.2V |
| Weight of powder obtained: | 71.5G. |
| Metallic content before heat treatment: | 76.44% |
| Metallic content after heat treatment: | 95.48% |
| Average energy consumption: | 4 Kwh/kg (A.C.) |

EXAMPLE II

| | |
|--|------------------------|
| Quantity taken: | 4 kg (-100 mesh) |
| Current passed: | 100 amp |
| Current density: | 10 amp/dm ² |
| Duration: | 42 hours |
| Cell voltage: | 3.7 to 3.2V |
| Electrolyte: | 40% NaOH (W/V) |
| Weight of iron powder obtained: | 2.6 kg |
| Maximum temperature during electrolysis: | 55°C |
| Metallic content: | 93.8% |

EXAMPLE III

| | | |
|---------------------------------|----------------|------------------------|
| Quantity taken : | -80 + 150: | 120 g |
| | -150 | 150 g |
| | Total | <u>270 g</u> |
| Current passed: | | 10 amp |
| Current density: | | 10 amp/dm ² |
| Electrolyte: | | 40% NaOH (W/V) |
| Duration: | | 2 hours |
| Cell voltage: | | 3.2V (average) |
| Weight of iron powder obtained: | -80 150 -85 g. | |
| | -150 | 110 g. |

Iron powder -80 150 obtained 101% of initial content
 Iron powder -150 mesh obtained 103% of initial content
 Metallic content:

| | |
|------------|-----|
| -80 +150 | 93% |
| - 150 mesh | 95% |

The following are the main advantages:

(1) The mill scale and the like material need not be brought into solution for electrolytically obtaining iron powder from the same.

(2) A large quantity of the mill scale which is otherwise thrown as a waste in sheet rolling and wire and rod drawing and other similar operations can be converted to electrolytic iron powder which will be very competitive and economical due to the fact that while energy consumption is the same for this and the conventional process, handling cost, raw materials and maintenance cost are much lower than the usual electrolytic process.

(3) The electrolyte can be reused a number of times (at least 10 cycles) with only a loss due to handling. Energy consumed are comparable with conventional process. Since most other unit processes are not involved, the process cost is more economical than the conventional electrolytic process.

(4) The process lends itself for ready scaling up so that high amperage cells can easily be employed for the process. The temperature rise etc., due to passage of large current is within limits since the current concentration is kept constant.

Summary

This invention relates to the production of iron powder by direct reduction of mill scales and the like obtained from steel rolling mills. Reducing the mill scale and the like by simple electrochemical reduction in alkaline medium eliminates the intermediate steps of dissolving the iron compound followed by electrolysis of the resulting solution. Copper, mild steel, nickel or nickel plated mild steel container is used as the cell and the mill scale and the like kept as a sediment at the bottom of the cell. The cell is made as the cathode and a mild steel, nickel plated mild steel, nickel or stainless steel mesh or perforated sheet mounted on an insulative frame, parallelly disposed over the bed of the powder so as to facilitate uniform current distribution serves as the anode. At the end of the reduction the iron powder is taken out of the cell, washed free from electrolyte stabilised and dried. The conversion efficiency is almost 100% and current efficiency ranged from 85 to 90%. In order to improve the quality of the iron powder and to make it soft it is given an annealing treatment in a hydrogen or dissociated ammonia atmosphere for durations varying between 10 minutes and 1 hour and at temperatures between 750° and 1000°C.

We Claim :

1. A process for the electrochemical production of iron powder from mill scale produced during rolling operations in steel rolling mills or materials of similar nature, the process comprising of direct electrochemical reduction of the scales or materials of similar nature on a metal substrate such as mild steel, copper, stainless steel, nickel or nickel plated mild steel, the container itself being used as the cathode, with an anode of mild steel, nickel plated mild steel, nickel or stainless steel wire mesh disposed parallelly over the bed of the mill scale or materials of similar nature and mounted on a frame so that while immersed in an electrolyte over the bed of mill scale or materials of similar nature facilitates uniform distribution of current.

2. A process as claimed in Claim 1 wherein mill scale or materials of similar nature are converted into iron powder by direct electrochemical reduction using an electrolyte of an aqueous solution of sodium, potassium or lithium hydroxide of strength between 5 and 50% (W/V) preferably 40% solution at a current density of 5-50 amp/dm² preferably at 10 amp/dm² and at laboratory temperatures.

3. A process as claimed in Claims 1 and 2 wherein the size of the iron powder after reduction is controlled by choosing the same or very near mesh size of the iron oxide scales or materials of similar nature.

4. A process as claimed in Claims 1 to 3 wherein the alkali electrolyte is recovered from the cell and reused by making good the loss due to drag out and handling.

5. The iron powder obtained by direct electrochemical reduction by the process claimed in Claims 1 to 4 is given a stabilising treatment with 2 to 3% soap solution or 0.1 to 1% potassium dichromate solution.

6. The iron powder produced by the direct electrochemical reduction process as claimed in Claims 1 to

5 is given a further heat treatment in an atmosphere of hydrogen or dissociated ammonia at a temperature ranging between 750 and 1000°C for a duration varying between 10 minutes and 1 hour.

7. A process for production of iron powder from mill scale or materials of similar nature by direct electrochemical reduction process and method of stabilising and heat treating the same substantially as hereinbefore described.

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Dated this 2nd day of December 1970.