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(54) PRODUCTION OF PURE IRON POWDER FROM PICKLING SOLUTIONS

(57) The present invention relates to a process for obtaining pure elemental iron which has high metalization ratio from the acid solutions obtained as a result of solublizing the iron-containing materials or surface treatments which are applied to iron-containing materials, particularly to steel materials and flat steel. In preferred embodiments of the invention, the process further comprises recovery of the acid from the waste acid solutions from the pickling processes.

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Description

Technical Field

[0001] The present invention relates to a method for producing pure iron powder from acidic solutions formed as a result of acidic pickling which is performed during surface treatment of iron-containing materials. More particularly, the invention relates to a method for the recovery of iron compounds from acidic solutions formed after the pickling procedure, treatment of the same in a specific process, and obtaining of pure iron with high metalization ratio.

Prior Art

[0002] The flat steel products which are used in automotive, white goods, electricity pylons, barriers etc. are usually surface cleaned acidically prior to coating with different metals (zinc, nickel, chromium, etc.), so called galvanization, in order to provide a longer service life. Apart from that, coating of steel and iron based sheet metals, bolts, nuts and wires having different purposes is an application used prevalently.

[0003] In the case of presence of grease, dirt or rust from previous processes on the steel materials to be coated, a successful coating can not be accomplished. Besides, pickling is applied prior to the galvanization in order to provide better adhesion of paint or coating on the steel material. Therefore, said steel materials are exposed to surface treatment prior to the galvanization just as all of the coating processes.

[0004] "Pickling", which is also known as the acidic surface cleaning stage, is performed in order to provide a clean and standart surface to the steel by way of cleaning surface of the same by solubilizing the oxide layer on the surface in an acidic bath (HCl, H_2SO_4). In the past, sulfuric acid baths were used commonly for the purpose of pickling in iron & steel industry, but as from 1960s, hydrochloric acid (HCl)-containing baths have started to become widespread with the aim of obtaining the product with more quality and more homogenized surface. Hydrochloric acid (HCl) is a particularly preferred acid bath due to the fact that it provides obtaining of a faster result, consuming low amount of acid and its pyrometallurgical regeneration is easier and more economic. 0.30 kg HCl is being used for 1 ton of steel during pickling.

[0005] The waste solution, which is also called spent acid, formed following the pickling applied for the surface cleaning of steel sheets is an iron rich solution. Beside this, said solution may contain hydrochloric acid, metal ions which are present in steel composition and soluble in HCl as well as certain amounts of zinc ions if an incorrect recovery is carried out.

[0006] There are variety of reactions occuring depending on the acid bath used in pickling and the structure of oxide which is formed on the surface of the iron. The pickling solutions formed as a result of the reactions with hydrochloric acid vary in very wide ranges in composition, and establishing the method to be applied for recovering of these solutions is quite difficult. The methods of recovering the acidic cleaning solutions are gathered in two groups. The first one is the recovery of acid and the second one is the recovery of the metal formed in the acid. The methods that are used for the acid recovery or regeneration are electrodialysis, diffusion dialysis, membrane distillation, evaporation and spray drying. For the recovery of metal, methods such as extraction, retardation, ion exchange and crystallization are used.

[0007] Recovery of acid and also iron compounds from acidic pickling solutions has been the focus of interest from the beginning of 1900s since it has an economical value. For instance, it is foreseen in GB 190300423-A that alkaline-earth metal carbonates to be added into the medium of the pickling bath including hydrochloric acid or sulphuric acid in order to recover the acid and the iron oxide.

[0008] An attempt regarding the recovery of iron compounds from a pickling solution containing $FeSO_4$ has been disclosed in GB 656,003. The process used herein involves the steps of gathering iron vitriol and water with a reductive agent such as sodium amalgam, and ultimately recovering the iron by precipitating. However, nowadays, because of environmental issues, application of this process is costly and dangerous for health since it does not bring a solution for pickling that uses HCl acid bath and it uses a reductive agent which makes use of mercury.

[0009] GB 1,219,674 discloses the reduction of iron oxide compounds (Aman oxide) by way of treating them with hydrogen by heating at high temperatures up to 1200 °C, preferably between 860-1200 °C, followed by sintering. However, sintering is a major problem in obtaining pure iron and flow paths can easily be clogged in dynamic systems such as fluidized bed. Moreover, sintered product is not preferred and it needs to be grinded.

[0010] On the other hand, obtaining a high metallizing ratio in the reduction of iron oxide compunds with hydrogen is a significant problem. In order to have an economical value, elemental iron should have high purity (>%99). Since the kinetics of reduction reactions depend on the diffusion of the reductive substance, pure iron is hard to obtain at high ratio, or long term treatment is essential, when the reaction occurs within the fixed bed reactors or other conventional equipments. In the present invention, a decomposition step is carried out at the first stage in a fluidized bed for the recovery of the acid in the spent acid composition while pure iron oxide (Fe_xO_y) is obtained from the iron-containing compounds ($FeCl_2$ and low amount of $FeCl_3$) formed in the spent acid, and HCl is obtained as the spent product. The second process step within the scope of the method is based on reduction of pure iron oxide (Fe_xO_y) compounds in a fludized bed system with hydrogen and/or CO-like reductant gas. Due to the fact that the final products of the reactions occured in this process are pure iron (Fe) and water vapor, it is possible to produce pure iron powder which has high metallizing ratios (>%99) without causing any environmental waste. While the particle size of pure iron oxide (Fe_xO_y) can be controlled by the parameters such as processing temperature, amount of the seed material and retardation time, it is possible to reduce the size of pure iron oxide particles by using the fact that iron oxide particles (Fe_xO_y) can be grinded easily. The aim of the invention is to obtain the acid and pure iron from pickling solutions in a short time with the desired quality and low cost, thereby minimizing the problems and limitations of the foregoing prior art. These objectives are achieved through a method as disclosed in claim 1.

Brief Description of the Invention

[0011] The present invention provides a process for obtaining pure iron from the acidic solution of a pickling process wherein an iron-containing material, particularly steel is surface treated. The process basically comprises the following steps:

- treating the iron-containing material with an acid solution (for the purpose of removing the oxide layer present on the surface or preparing for another process or obtaining a proper solution just for this process),
- solubilizing with acid (surface cleaning) followed by applying thermal decomposition to iron chloride compounds present in said solution,
- seeding by addition of iron oxide to the medium during thermal decomposition and obtaining layered Fe_xO_y compounds,
- contacting the obtained layered Fe_xO_y compounds with a reductant substance in a fluidized, fixed or rotating bed and reduction of the iron compounds, and
- cooling the pure iron powder at the end of the reduction by preventing re-oxidization of the powder, and obtaining iron powder of commercial grade.

[0012] The acid used in the process according to the present invention is preferably hydrochloric acid (HCl). Said thermal decomposition can be carried out preferably in a fluidized bed and at a temperature between 500 °C and 1000 °C.

[0013] In the reduction step of the process which is for reducing Fe_xO_y compounds, preferably H_2 or CO is used, more preferably H_2 is used as a reductant. Besides, removal of the water occurring in this step is particularly preferred. Said reduction can be carried out at a temperature above 500 °C as mentioned above. However, in order to minimize the negative effects of sintering, it has been observed that the reduction can be carried out at temperatures of between 600-800 °C, more preferably about 650 °C. The reductant used herein may comprise H_2/N_2 gas mixture having a volumetric ratio of higher than 1:1, more preferably 2:1 or more.

[0014] It has been found that obtaining Fe_xO_y particles by way of seeding during formation of Fe_xO_y compounds in thermal decomposition has certain advantages. Ultimately, due to this reason, elemental iron is obtained in a layered structure. Said Fe_xO_y particles treated with reduction have the preferred particle size of between 300 μm and 1000 μm, more preferably between 300 μm and 600 μm. Thus, the additional operations affecting quality of the material in the negative way such as grinding are eliminated.

Brief Description of Drawings

[0015]

Figure 1 is the SEM image of the Fe_xO_y particles which are obtained by seeding in the thermal decomposition step of the process according to the present invention.

Figure 2 shows the phase stability diagram which is dependent on the partial pressure of hydrogen and the ambient temperature.

Figure 3 is the diagram showing the temperature dependent H_2/N_2 ratio and % metalization.

Figure 4a presents the SEM image of the resultant iron particles of the reduction procedure which was carried out for 60 minutes wherein the volumetric ratio of H_2/N_2 was 2:1 at 500 °C.

Figure 4b presents the SEM image of the resultant iron particles of the reduction procedure which was carried out for 60 minutes wherein the volumetric ratio of H_2/N_2 was 2:1 at 1000 °C.

Detailed Description of the Invention

[0016] Within the scope of the present invention, a process for the production of pure iron powder from the waste acidic solutions formed at the end of the acidic (HCl) pickling treatment which is applied during surface treatments of iron-containing materials, particularly steel materials is disclosed. Said process optionally comprises the steps of regeneration and recovery of the spent acid used in the process.

[0017] Within the scope of said method, initially Thermal Decomposition is applied to the waste acidic solution formed as a result of the acidic cleaning which is applied to the metallic materials, and finally, iron oxide compounds (Fe_xO_y) are obtained. Then, pure iron powder is obtained with high value by carrying out reduction of Fe_xO_y compounds via a reductant in the fluidized bed.

[0018] Some of the reactions occured during pickling procedure applied to metallic materials which constitute first step of the process are as follows:

$$Fe_2O_3 + Fe + 6HCl \rightarrow 3FeCl_2 + 3H_2O$$

$$Fe_3O_4 + Fe + 8HCl \rightarrow 4FeCl_2 + 4H_2O$$

$$FeO + 2HCl \rightarrow FeCl_2 + H_2O$$

$$2Fe_3O_4 + 18HCl + 1/2O_2 \rightarrow 6FeCl_3 + 9H_2O$$

$$6FeCl_3 + 3Fe \rightarrow 9FeCl_2$$

[0019] The oxides on the surface of steel or iron-containing material treated with a pickling procedure are eventually cleaned and the material is prepared for subsequent surface treatments. In the process bath, there exist usually the used HCl, iron ions, zinc ions and iron chloride compounds. There exist in the composition of the solution also metal chlorides coming from the steel structure, which can be soluble in acid.

[0020] In the pickling process carried out within the scope of the present invention, preferably 60-200 g/l Fe^{2+} ions and 25-100 g/l HCl can be present. As a result of the pickling procedure, iron chloride compounds in general are obtained in $FeCl_2$ (and partially $FeCl_3$) form.

[0021] It is aimed in the second step of the process according to the invention to obtain iron oxide compounds by way of applying a Thermal Decomposition procedure to the pickling solution containing iron chloride and HCl. Some of the reactions occured during this application are as follows:

$$4FeCl_2 + 4H_2O + O_2 \rightarrow 8HCl_{(gas)} + 2Fe_2O_3$$

$$6FeCl_3 + 9H_2O \rightarrow 18HCl_{(gas)} + 2Fe_3O_4 + 1/2O_2$$

$$2FeCl_3 + FeCl_2 + 3H_2O \rightarrow 8HCl_{(gas)} + Fe_3O_4$$

[0022] During thermal decomposition, HCl and iron chloride-containing dirty acid solution decomposes, and as a result, HCl is obtained along with Fe_xO_y compounds as the side product. In preferred embodiments of the invention, it is possible to accelerate the decomposition reactions and facilitating removal of HCl gas by way of carrying out this operation in a fluidized bed. It has been observed during the operation that the reactions can be carried out ideally when the temperature is preferably between 750 °C and 950 °C, and more preferably between 850 °C and 900 °C.

[0023] The invention, in another aspect, may comprise an additional process step besides obtaining of pure iron which allows the recovery of gaseous HCl occurring after thermal decomposion in order to use it again in the pickling bath. Accordingly, the regenerated gaseous acid can be removed from the medium, cooled and stored by way of conventional techniques, or it can be fed back to the pickling procedure. It has been observed that gaseous regenerated acid can be recovered more easily and efficiently if the thermal decomposition is carried out in a fluidized bed. The regenerated acid, for instance, can be seperated from iron oxide particles by way of drawing it into a cyclone by means of a fan. Afterwards, acid vapor comes to a venturi and its temperature can be decreased till 100 °C. For instance, a ready-to-use acidic solution can be formed by spraying water onto the regenerated acid which can be taken into absorbers.

[0024] At the third step of the process according to the present invention invention, reduction of Fe_xO_y compounds is carried out by using a reductant, and pure iron is obtained in elemental form. Since several problems has been encountered in carrying out this operation, there has been no improvement with the commercial processes (reduction in fixed bed systems) in prior art going beyond obtaining of the iron oxide compounds and commercialisation could not be achieved with an efficient process up to now. Within the scope of the present invention and in the studies for overcoming these problems, it is noted that the reactions of Fe_xO_y with a reductant are limited kinetically with a diffusion barrier. Besides, the reduction reactions are largely affected with the temperature and the ratio of reductant/carrier gas. It has been observed from the experiments that, even when the temperature was increased up to 1100 °C and the ratio of reductant (H_2)/carrier (N_2) was 1:1, the metalization ratio has stayed in the level of 21-22%. Moreover, sintering is a major problem and FeO film layer formed in the reduction step has significant role in sintering.

[0025] The inventors have found that the abovementioned diffusion limitation can be eliminated by using fluidizied bed at the reduction step. Since the contact surface of iron oxide particles with the reductant gas has been increased, a considerable increase in the efficiency has been observed. However, even though it has positive effect, it has been observed that the desired ratio of metalization could not be achieved and sintering is still a problem. To overcome these problems, the inventors have carried out a seeding procedure in thermal decomposition step and obtained the layered iron oxide compounds as shown in Figure 1. The seeding can be carried out by addition of iron oxide seeds to the decomposition reaction medium. It has been unexpectedly observed that this layered structure has eliminated particularly the diffusion barrier problem, enhanced the reduction kinetics of Fe_xO_y compounds and it plays a significant role in obtaining the metalization at a higher ratio (>%99 Fe).

[0026] Accordingly, the iron oxide (Fe_xO_y) compounds which are formed via seeding at the end of the decomposition, are being contacted with a reductant in a fluidized bed and pure iron powder (Fe) is eventually obtained. Said reductant is preferably H_2 or CO, more preferably H_2 gas. However, reductant gases which are known in the prior art like CH_4 can also be used. In the case of H_2 usage as a reductant, the reduction of Fe_xO_y compounds in the fluidized bed is basically carried out in three steps. Said reaction steps are as follows:

$$3Fe_2O_3 + H_2 \rightarrow 2Fe_3O_4 + H_2O$$

$$2Fe_3O_4 + 2H_2 \rightarrow 6FeO + 2H_2O$$

$$6FeO + 6H_2 \rightarrow 6Fe + 6H_2O$$

[0027] Accordingly, the total reaction is as follows:

$$Fe_xO_y + yH_2 \rightarrow xFe + yH_2O$$

[0028] In Figure 2, the phase stability diagram which is dependent to the partial pressure of hydrogen and the ambient temperature is shown. It is possible to remove the water vapor which is the product of the reaction from the medium so as to decrease the partial pressure of hydrogen and increase the reaction rate. The water formed in the reaction can be removed by dewatering. Process is accelerated due to the fact that the only gaseous product is water vapor in the reaction and it can be removed by condensation. Dewatered gas can be fed back to the system and continuation of the reactions can be ensured. A considerable increase in the % metalization ratio has been noted in the case of carrying out the abovementioned reduction process at a temperature of 600°C or more. Besides, an increase in the % metalization ratio has again been observed in the case that the volumetric ratio of H_2/N_2 is higher than 1:1, and more preferably higher than 2:1 when hydrogen/nitrogen mixture was fed to the reduction medium of a reduction gas system. These effects can clearly be seen from the experimental results given in Figure 3. Therefore, it is preferred in the reaction conditions where best effects were observed that the temperature is between 650 °C and 1000°C in the reduction conditions and the volumetric ratio of H_2/N_2 is higher than 1:1 in the case of using H_2/N_2 reductive system. Besides, it has been noted that sintering is unexpectedly minimized when the size of Fe_xO_y particles treated with reduction is kept between 300 μm and 600 μm, and in this case reductive diffusion doesn't cause a limitation for reaction kinetics.

[0029] Figure 4a presents the SEM image of the resultant iron particles obtained through the reduction procedure which has been carried out for 60 minutes wherein the volumetric ratio of H_2/N_2 was 2:1 at 500 °C. In this experiment, 46% metalization was achieved.

[0030] Figure 4b presents the SEM image of the resultant iron particles obtained through the reduction procedure which has been carried out for 60 minutes wherein the volumetric ratio of H_2/N_2 was 2:1 at 1000 °C. In this experiment, %99.98 metalization was achieved.

[0031] Both of the experiments show that temperature has significant effect on the metalization ratio. Besides, considering Figures 4a and 4b together, it has been clearly observed that the reduction proceeds from outside to inside topochemically. Due to the structure of Fe_xO_y in layered form on the seeding material in acid regeneration system (at thermal decomposition step), the same form was observed in the reduced structure as well. Due to the fact that this layered structure facilitates the gas transition during reduction and removal of water which is product of the reaction, formation of any diffusion barrier that blocks or obstruct reduction in the experimental studies has not been observed. It is possible to keep the reduction time shorter than 60 minutes with the effect of this structure. In the case of using pure hydrogen, it becomes possible to shorten the process time further.

Claims

1. A process for obtaining pure iron from an acidic solution of a pickling process wherein an iron-containing material is surface treated, said process comprises the steps of:

    - solubilizing of the iron-containing material with an acidic solution,
    - applying thermal decomposition to iron chloride compounds formed in said solution following the solubilizing,
    - seeding by adding iron oxide to the medium during thermal decomposition and obtaining Fe_xO_y compounds in layered form,
    - contacting the so formed layered Fe_xO_y compounds with a reductant material in a fluidized bed, and reduction of iron compounds, and
    - obtaining pure iron powder as a result of the reduction.

2. A process according to Claim 1, wherein the acidic solution comprises hydrochloric acid (HCl).

3. A process according to Claim 1, wherein the iron-containing material is flat steel.

4. A process according to Claim 1, wherein the thermal decomposition is carried out in a fluidized bed or a rotating furnace.

5. A process according to Claim 1, wherein the temperature in the thermal decomposition treatment is between 750 °C and 950 °C.

6. A process according to Claim 4, wherein the process further comprises obtaining regenerated HCl solution by drawing of HCl gas from the fluidized bed and cooling it in the thermal decomposition step.

7. A process according to Claim 1, wherein the reductant material is H_2 or CO.

8. A process according to Claim 7, wherein the reductant material is H_2.

9. A process according to Claim 1, wherein the process comprises the removal of water which is formed during reduction of the iron compounds.

10. A process according to Claim 1, wherein the reduction is carried out at a temperature between 500 °C and 1000 °C.

11. A process according to Claim 10, wherein the reduction is carried out at a temperature between 600 °C and 800 °C, more preferably about 650 °C.

12. A process according to Claim 1, wherein H_2 is fed as reaductant along with N_2 as a carrirer and wherein the volumetric ratio of H_2/N_2 is higher than 1:1.

13. A process according to Claim 12, wherein the volumetric ratio of H_2/N_2 is higher than 2:1.

14. A process according to Claim 1, wherein the particle size of Fe_xO_y compounds treated with the reduction is between 300 μm and 600 μm.

15. Layered Fe_xO_y particles which are obtained according to the process of Claim 1.

16. Layered Fe particles which are obtained according to the process of Claim 1.

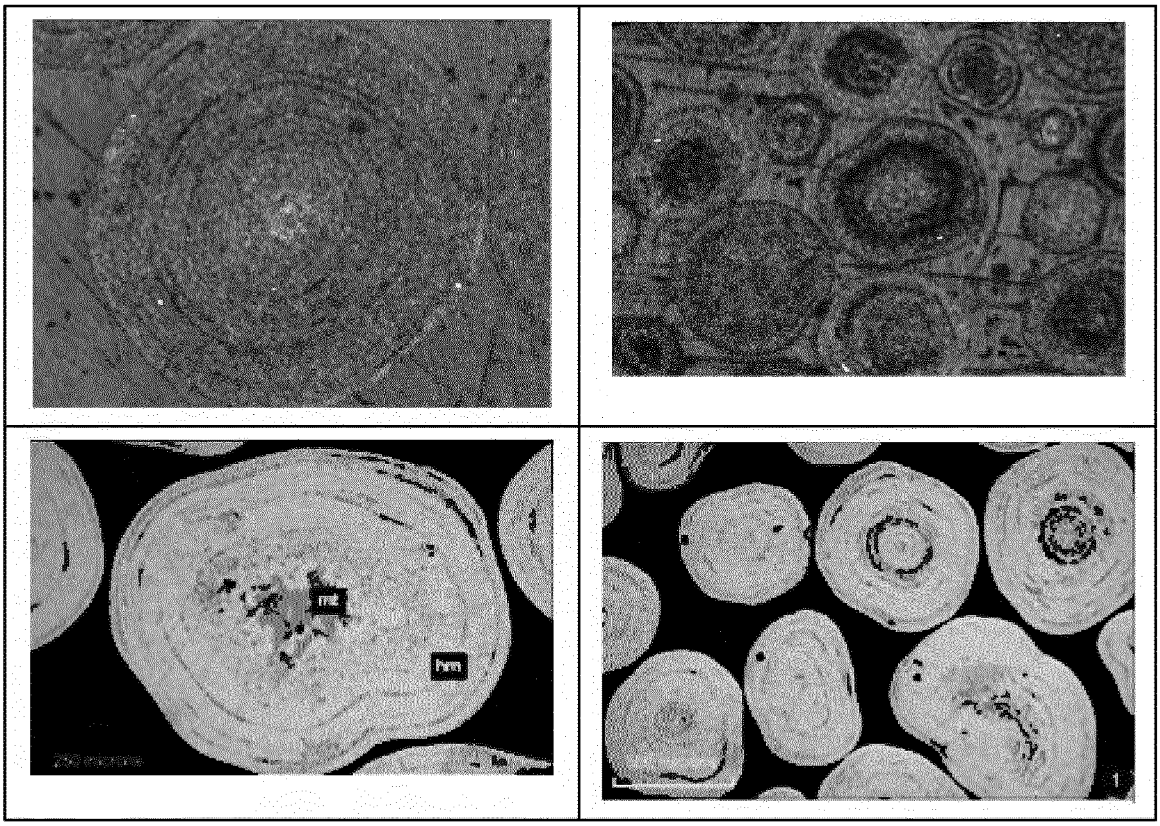

Figure 1

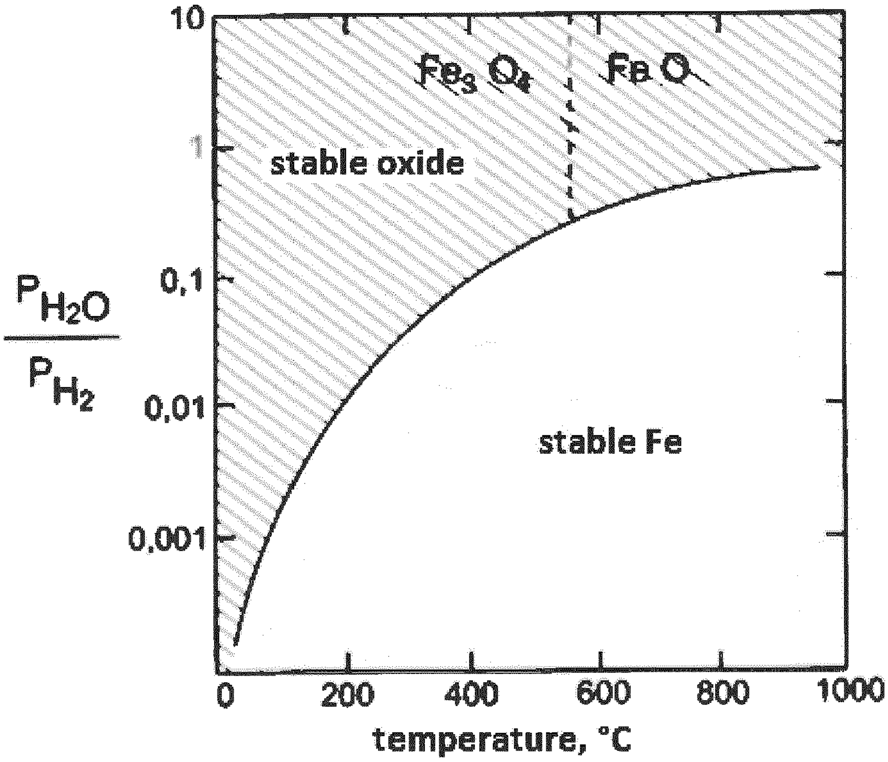
10
1
0,1
0,01
0,001
$\frac{P_{H_2O}}{P_{H_2}}$
Fe3 O4
Fe O
stable oxide
stable Fe
0
200
400
600
800
1000
temperature, °C

Figure 2

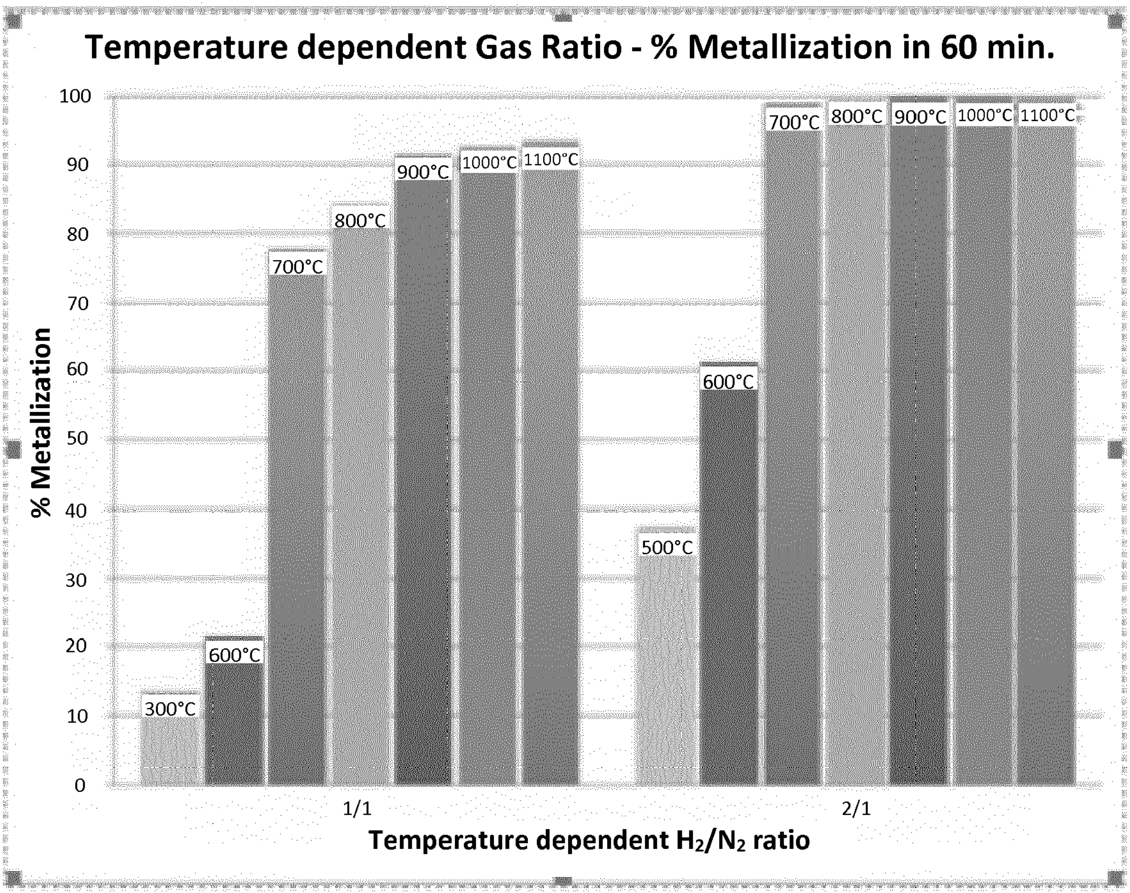
Temperature dependent Gas Ratio - % Metallization in 60 min.
% Metallization
100
90
80
70
60
50
40
30
20
10
0
300°C
600°C
700°C
800°C
900°C
1000°C
1100°C
500°C
600°C
700°C
800°C
900°C
1000°C
1100°C
1/1
2/1
Temperature dependent H2/N2 ratio

Figure 3

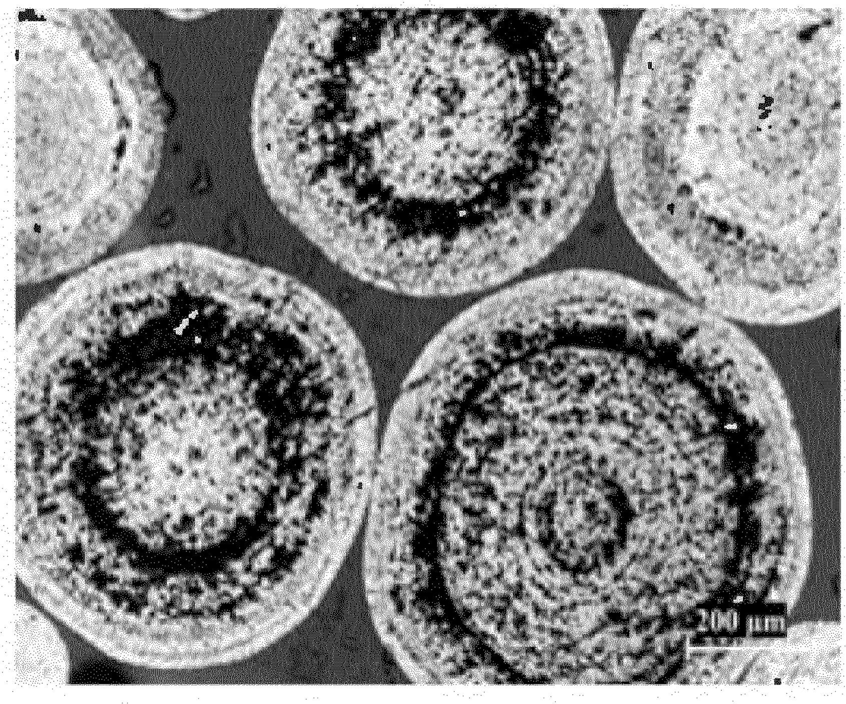

Figure 4a

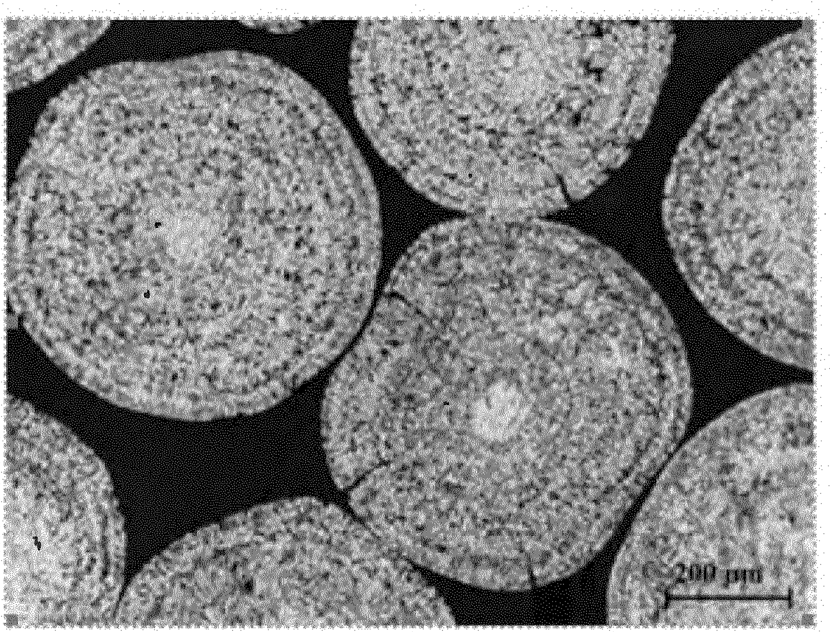

Figure 4b

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EUROPEAN SEARCH REPORT

Application Number
EP 17 16 2167

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The present search report has been drawn up for all claims

1

Place of search	Date of completion of the search	Examiner
The Hague	31 August 2017	Fodor, Anna

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO.

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