(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) **EP 2 687 611 A1**

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
22.01.2014 Bulletin 2014/04

(21) Application number: **12005250.1**

(22) Date of filing: **17.07.2012**

(51) Int Cl.:
***C21D 1/76** (2006.01)*
***C21D 9/56** (2006.01)*
***C21D 8/02** (2006.01)*
***C23C 2/02** (2006.01)*

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA ME

(71) Applicant: **Linde Aktiengesellschaft**
80331 Munich (DE)

(72) Inventors:
- **Foret, Pierre**
  80796 München (DE)
- **Murén, David**
  18 539 Vaxholm (SE)
- **Ritzén, Ola**
  18 494 Åkersberga (SE)
- **Wiberg, Sören**
  17 835 Ekerö (SE)

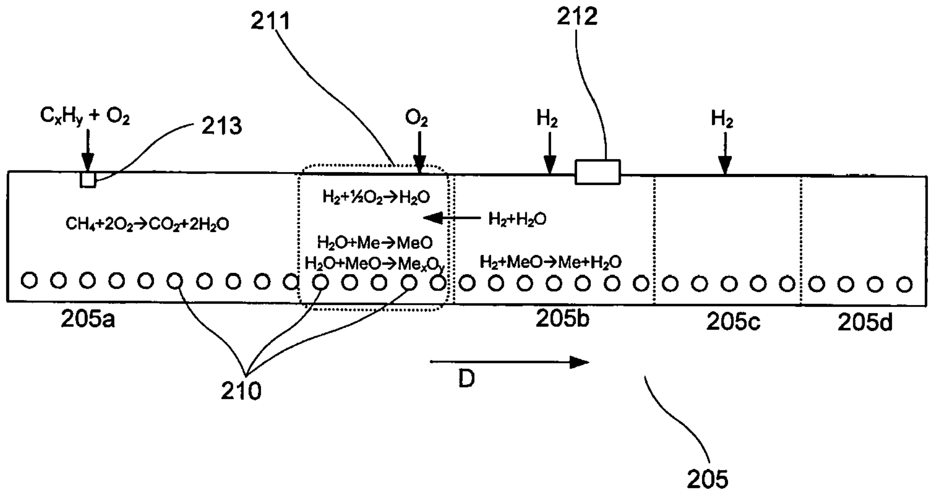
(74) Representative: **Gellner, Bernd**
Linde AG
Legal Services Intellectual Property
Dr.-Carl-von-Linde-Strasse 6-14
82049 Pullach (DE)

(54) Method and apparatus for controlling surface porosity of metal materials

(57) Method for controlling surface porosity of a metal material (210), wherein the metal material is first heat treated under an oxidizing atmosphere, so that metal oxide is formed in the metal material, after which the metal material is held under a reducing atmosphere, so that the said oxide is at least partly reduced whereby pores are formed in the metal material.

The invention is characterized in that the metal material is brought through, firstly, an annealing device (205a), in which the said heat treatment at least partly takes place and in which the metal material is subjected to the oxidizing atmosphere, and, secondly, a reduction device (205b) in which the metal material is subjected to the said reducing atmosphere, in that the metal material is not subjected to another atmosphere, apart from said oxidizing and said reducing atmospheres, between the oxidizing and reducing atmospheres, and in that gaseous H_2O is caused to be present in a downstream section (211) of the annealing device through which the metal material is conveyed before reaching the reduction device.

Fig. 3



Printed by Jouve, 75001 PARIS (FR)

Description

[0001] The present invention relates to a method and an apparatus for controlling surface porosity of metal materials. More precisely, it relates to such a method and such an apparatus for producing a metal material product with a controlled porous surface.

[0002] The manufacture of many types of metal products, such as various types of steel products, conventionally comprises the processing steps of annealing and pickling, the purpose of the latter being to remove scale formed on the material surface during for example heating and/or quenching. During pickling, up to 0.5-1% of the metal material can be lost in the removed scale, which is a problem. Also, pickling is expensive and potentially harmful to the environment.

[0003] In order to avoid the pickling step, reduction and cooling can take place under reducing atmosphere, such as described in WO 02/04145.

[0004] Another problem is that the surface characteristics of many metal products produced by a method involving heat treatment are often less than perfect in terms of roughness, topography, adhesion, catalytic properties, tribology, etc. This may result in, for example, the surface displaying poor performance in subsequent processing steps such as drawing, rolling, painting, galvanizing, skin pass rolling and polishing. Furthermore, the product surface may need additional surface processing before it can be used as a finished product in a particular application, for example as a part in a heat exchanger.

[0005] One example is that, after acid pickling, the surfaces of many steel products are often flat on the material grains but include ditches along grain boundaries. The result is that the roughness of the surface (the so called RA value) will be adequate, but lubrication will be poor during subsequent processing steps, such as wire drawing, cold rolling and skin pass rolling.

[0006] EP1935508 describes a general method for creating a surface with predetermined characteristics on a metal product, specifically a porous surface. The material is firstly heat treated, whereby a surface layer is formed containing non-metal compounds, after which a reducing atmosphere is used to partly remove the said surface layer, whereby pores are formed in the surface as a result of the material removal.

[0007] It would be desirable to achieve a simple, cost efficient, environmentally friendly method with low space requirements, capable of creating predetermined attractive surface properties in a metal product produced using heat treatment.

[0008] These and other problems are solved by the present invention.

[0009] Thus, the invention relates to a method for controlling surface porosity of a metal material, wherein the metal material is first heat treated under an oxidizing atmosphere, so that metal oxide is formed in the metal material, after which the metal material is held under a reducing atmosphere, so that the said oxide is at least partly reduced whereby pores are formed in the metal material, and is **characterized in that** the metal material is brought through, firstly, an annealing device, in which the said heat treatment at least partly takes place and in which the metal material is subjected to the oxidizing atmosphere, and, secondly, a reduction device in which the metal material is subjected to the said reducing atmosphere, in that the metal material is not subjected to another atmosphere, apart from said oxidizing and said reducing atmospheres, between the oxidizing and reducing atmospheres, and in that gaseous H_2O is caused to be present in a downstream section of the annealing device through which the metal material is conveyed before reaching the reduction device.

[0010] In the following, the invention will be explained in closer detail, partly in connection with the appended drawings, whereof:

Figure 1 schematically illustrates a conventional process line for producing wire;

Figure 2 schematically illustrates the process line of figure 1, but after application of a method according to the present invention, including the industrial furnace as viewed in figure 3;

Figure 3 schematically illustrates an industrial furnace according to the present invention;

Figure 4 is a graph illustrating an exemplary distribution of basic compounds in a finished metal material product (Y axis), as a function of distance from its surface (X axis), after application of a method according to the present invention; and

Figure 5 is a diagram displaying the phase fields of Fe and various Fe oxides and their interrelation with partial pressures and temperature.

[0011] Figure 1 illustrates a conventional process line for producing wire. In a first heating step 101, metal material is heated. Thereafter, in a hot roll mill step 102 and a roll block step 103, the material is shaped, after which it passes a finishing block step 104. Then, the material enters an annealing and cooling step 105, in which it is first annealed in an annealing step 105a and then cooled in a cooling step 105b. The resulting wire rod 106 is then brought through pickling 107, washing 108 and drying 109 steps in order to obtain a finished wire product.

[0012] In such a process, the possibility to control the surface characteristics of the metal material is limited. The normally used acid pickling merely removes the scale, formed during preceding processing steps, and chromium depleted zones - it does little to optimize the surface properties such as roughness, topography, adhesion, catalytic properties, tribology and so on.

[0013] In a typical conventional process, the annealing step 105a is an open flame furnace, and the pickling 107 is done using different acids, such as a mixture of HNO_3 and HF. The process can be of batch type, in which a batch of metal material is processed at a time, or continuous. In either case, the cooling step 105b may comprise a quenching step, such as a water quenching step. The cooling step 150b may also comprise an air or water cooling step.

[0014] The annealing step 105a is typically arranged to heat the metal material to annealing temperatures under normal open flame combustion. As a consequence, scale is produced which then needs to be removed in the pickling step 107.

[0015] Figure 2 illustrates a process line similar to the one shown in figure 1, including a first heating step 201, a hot roll mill step 202, a roll block step 203 and a finishing block step 204. The process line illustrated in figure 2 is for producing stainless steel wire, but it is realized that the principles disclosed herein are equally applicable to other products and/or other metal materials. Examples of such materials include various types of high alloyed steels, such as tool steel, speed steel and various special steels, and alloyed copper materials. Examples of such products include wire rod, strips and plates.

[0016] After the initial processing steps 204, the metal material 210 is transported through an industrial furnace device 205, which transportation can be carried out in a way which is conventional as such in order to achieve a batch-wise or continuous processing of the metal material 210.

[0017] According to the invention, the metal material 210 is first heat treated under an oxidizing atmosphere, so that metal oxide is formed in a surface layer of the metal material 210, after which the metal material 210 is held under a reducing atmosphere, so that the said oxide is at least partly reduced and whereby pores are formed in the metal material 210. By controlling the oxidizing atmosphere and the reducing atmosphere, as well as holding times and temperatures in the various zones in the furnace device 205, the surface porosity of the metal material 210 can be controlled.

[0018] Moreover, according to the invention, the metal material 210 is brought through, firstly, an annealing device 205a, in which the heat treatment of the metal material 210 at least partly takes place and in which the metal material 210 is subjected to the oxidizing atmosphere, and, secondly, a reduction device 205b in which the metal material 210 is subjected to the said reducing atmosphere.

[0019] The annealing device 205a is heated by combusting a gaseous, liquid or solid phase fuel with an oxidant in the form of air or oxygen-enriched air, such as an oxidant containing at least 85% oxygen, preferably at least 95% oxygen. Preferably, at least one burner 213 with an open flame is used. The supply of fuel and oxidant to the annealing device is indicated in figure 3 by $C_xH_y+O_2$. The said combustion results in carbon dioxide and water:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O.$$

[0020] According to the invention, the metal material 210 is not subjected any another atmosphere, apart from said oxidizing and said reducing atmospheres, between the oxidizing and reducing atmospheres. In other words, the annealing device 205a and the reduction device 205b are connected in a gas-tight or essentially gas-tight manner, sharing the same interior volume, and the metal material 210 is conveyed from the annealing device 205a to the reduction device 205b without coming into direct contact with any other atmosphere than the ones prevailing in said devices 205a, 205b there between. It is preferred that the annealing device 205a and the reduction device 205b, and possibly also the cooling device 205c and possibly the quenching device 205d (see below), are arranged as different sections of one and the same furnace chamber. However, it is also possible that some type of intermediate arrangement, through which the metal material 210 is conveyed between the annealing 205a and the reduction 205b devices, is present, as long as there is no exposure of the metal material 210 to an external atmosphere.

[0021] The reduction device 205b is heated using a heating arrangement 212 arranged to heat the reducing atmosphere without introducing any oxidizing compounds into the reducing atmosphere, preferably arranged not to chemically interfere with the said reducing atmosphere at all. Examples of such heating arrangements include induction and direct electrical heaters, as well as radiation tubes. The compounds of the reducing atmosphere in the reduction device 205b can also be preheated before entering the device 205b.

[0022] Furthermore, according to the invention, gaseous H_2O water vapour, is caused to be present in a downstream section 211 of the annealing device 205a through which the metal material 210 travels before reaching the reduction device 205b. "Downstream" in this context refers to the travel direction D (see figure 3) of the metal material 210. In other words, the downstream section 211 is a section of the device 205a arranged just before the device 205b in the travel direction D of the metal material 210. The section 211 is preferably merely the part of the furnace chamber of the device 205a in which gaseous H_2O is present in substantial amounts, but the section 211 can also be partly separated from the rest of the chamber of the device 205a, using baffles or the like.

[0023] One preferred way of achieving such provision of H_2O in said downstream section 211 is that the reducing atmosphere in the reduction device 205b is caused to comprise H_2, and that the atmosphere of the reduction device is circulated counter-currently with respect to the travel direction D of the metal material 210, so that furnace gases are circulated counter-currently in relation to the travel direction D of the metal material 210 from the reduction device 205b into the annealing device 205a. Such counter-current circulation can also take place from the cooling section 205c (see below), especially if H_2 jets are used for cooling.

[0024] Hence, H_2 from the reducing atmosphere present in the reduction device 205b reaches the said downstream section 211 of the annealing device 205a as a consequence of said counter-current circulation of furnace gases. In this case, the water vapour is provided to the said downstream section 211 by supplying O_2 to the downstream section 211, which O_2 is caused to react with the H_2 arriving into the downstream section 211 of the annealing device 205a from the reduction device 205b:

$$H_2 + ½O_2 \rightarrow H_2O.$$

[0025] The combustion of H_2 from the reduction device 205b also utilizes the chemical energy in the hydrogen, improving the total efficiency of the process.

[0026] It is preferred that the reducing atmosphere in the reduction device 205b is constituted by essentially pure H_2, or H_2 with an addition of some inert gas, such as N_2. The reducing gases are preferably pre-heated and pressurized to maximize the reduction speed and uniformity. Moreover, the reducing gases are preferably re-circulated in the reduction device, and water and/or CO_2 are continuously separated off from the reducing gases, preferably by drying.

[0027] It is preferred that the O_2 supplied to the downstream section 211 is supplied via one or several lances, in the form of a gas containing at least 85% O_2, more preferably at least 95% O_2, rather in the form of industrially pure O_2. Such oxidant decreases the N_2 ballast as compared to, for instance, air, and increases efficiency. The same advantage applies to the use of a high oxygen oxidant as mentioned above.

[0028] It is also possible to supply H_2O to the downstream section 211 in other ways, such as for example directly to the said downstream section 211. One example is to, as a supplement or an alternative to the above described O_2 lancing, directly inject water steam or atomized water liquid into the downstream section 211.

[0029] It is preferred that the dew point in the downstream section 211 is at least +10°C, preferably between +20°C and +85°C.

[0030] The presence of H_2O in the downstream section 211 results in the formation of metal oxide in surface layers of the metal material 210 before leaving the annealing device 205a:

$$H_2O + Me \rightarrow MeO$$

$$H_2O + MeO \rightarrow Me_xO_y,$$

[0031] Wherein Me is the metal used, such as for example Fe, and x and y are suitable integers, depending on the metal used.

[0032] In the H_2O rich atmosphere of the section 211, the oxide scale formed in the surface layers of the metal material 210 will be oxidized further, to form the oxide in equilibrium with the water rich atmosphere, see figure 5.

[0033] For example, when the metal material 210 comprises Fe, Fe_3O_4 and FeO will oxidize further to form Fe_2O_3. The thus formed Fe_2O_3 will form a more porous scale, yielding a more porous surface structure when reduced in the reduction device 205b. Similar oxidation occurs for certain other alloying elements which may be present in the metal material 210, such as Cr, Ni and Mo.

[0034] In the reduction device 205b, the formed oxide will be reduced partially or completely, which results in a porous surface of the metal material 210. For example, surface properties which are suitable for lubrication for drawing a metal wire product can be achieved this way, or a surface which is suitable for galvanizing, or a surface with a desired aesthetic appearance.

[0035] The surface porosity characteristics of the final metal material product is controlled by regulating the oxide formation in the water rich downstream section 211 of the annealing device 205a, and the reduction of these oxides in the reduction device 205b, especially in terms of the temperatures, partial pressures and holding times in the downstream section 211 and the reduction device 205b. The exact combination of these parameters depends on the type of metal material to be processed and on the desired final product, and is well within the capabilities of the skilled person to determine. Furthermore, by controlling the H_2O concentration in the downstream section 211, the resulting oxidation, as described above, can be controlled precisely.

[0036] Depending on the type of metal material 210, it is preferred that the oxidizing atmosphere in the annealing device 205a is heated to a temperature which is at least 800°C, more preferably at least 1050°C, and at most 1300°C, more preferably at most 1250°C; that the atmosphere in the downstream section 211 is heated to a temperature which is at least 800°C, more preferably at least 1050°C, and at most 1300°C, more preferably at most 1250°C; and that the reducing atmosphere in the reduction device 205b is heated to at least 700°C, more preferably at least 800°C, and at the most 1300°C, more preferably at the most 1200°C.

[0037] It is preferred that the oxidizing atmosphere in the annealing device 205a has a content of O_2 which is between 0 and 10 % by weight.

[0038] Preferred holding times under the water rich atmosphere in the downstream section 211 are between 30 and 500 seconds, and in the reducing atmosphere in the reduction device 205b between 60 and 300 seconds.

[0039] Furthermore, if the metal material 210 contains Cr, which is preferred and as is the case for certain types of stainless steel, it is preferred that the dew point of the reducing atmosphere in the reduction device 205b is -20°C or less, since reducing conditions also for chromium oxides can then also be achieved.

[0040] As a matter of fact, the present inventors have discovered that by using a method according to the present invention on stainless steel containing chromium, the finished metal product will exhibit a relatively higher (A % higher, see figure 4) chromium content near the surface of the material, providing improved resistance to oxidation.

[0041] After having traversed the reduction device 205b, the metal material 210 is preferably conveyed to a cooling device 205c in which the metal material 210 is subjected to another reducing atmosphere. It is in this case preferred that the metal material 210 is conveyed from device 205b to device 205c without being subjected to any atmosphere apart from the reducing atmosphere in the reduction device 205b and the reducing atmosphere present in the cooling device 205c.

[0042] In the cooling device 205c, it is preferred that the temperature of the metal material 210, preferably its core temperature, is brought to below 400°C in the cooling device 205c.

[0043] It is preferred that the cooling device is also arranged to subject the metal material 210 to a reducing atmosphere, such as an atmosphere comprising H_2 with possible inert compounds, in order to avoid re-oxidizing. It is also preferred that such cooling is performed fast enough to obtain desired material properties, such as to achieve substantial suppression of the formation of carbides in the material. To this end, it is preferred that the cooling, reducing atmosphere is brought into contact with the metal material 210 under pressure and preferably in the form of gas jets directed onto the material 210.

[0044] An alternative or supplement to the gas jet cooling in device 205c, a water cooled tunnel can be used.

[0045] Finally, the metal material 210 may be conveyed to a quenching device 205d, which may also be an integrated part, like is possibly the case with the cooling device 205c, of the same industrial furnace apparatus 205 as devices 205a and 205b, preferably sharing the same furnace chamber space.

[0046] After the metal material 210 exits the furnace 205, it is finished 206, or can be processed in additional processing steps (not shown).

[0047] Using a method according to the present invention, the porosity of the final product surface can be optimized for a subsequent processing step, such as drawing, rolling, painting, galvanizing, skin pass rolling, polishing, or for application in a final product, such as a component in a heat exchanger or a fuel cell. The present process is environmentally friendly, energy efficient and can be embodied in a very compact manner, saving valuable space. It does not lead to any substantial loss of material.

[0048] Furthermore, such a method makes the conventional pickling step unnecessary, as well as associated processing steps. This is desirable, for a number of reasons. For example, salt bath pre-treatment gives rise to loss of material, high costs and environmental threats; neolytic pickling consumes electrical energy, gives rise to harmful waste and high costs; acid pickling involves the handling of harmful substances such as HF and HNO_3 and gives rise to emission of gases, such as NO_x, and scale sludge; scale breaking gives rise to loss of material, waste and high costs; and rinsing and brushing gives rise to contaminated waste water and high costs. All these things are unnecessary when producing a metal product according to the present invention.

[0049] Above, preferred embodiments have been described. However, it is apparent to the skilled person that many modifications may be made to the described embodiments without departing from the inventive idea.

[0050] For example, the present method may be equally well be applied to a process which, rather than steps 201, 202, 203 and 204, instead comprises other steps for heating, shaping and treating metal materials with the aim of obtaining some other type of final product.

[0051] Thus, the invention is not limited to the described embodiments, but may be varied within the scope of the enclosed claims.

Claims

1. Method for controlling surface porosity of a metal material (210), wherein the metal material is first heat treated under an oxidizing atmosphere, so that metal oxide is formed in the metal material, after which the metal material is held under a reducing atmosphere, so that the said oxide is at least partly reduced whereby pores are formed in the metal material, **characterized in that** the metal material is brought through, firstly, an annealing device (205a),

in which the said heat treatment at least partly takes place and in which the metal material is subjected to the oxidizing atmosphere, and, secondly, a reduction device (205b) in which the metal material is subjected to the said reducing atmosphere, **in that** the metal material is not subjected to another atmosphere, apart from said oxidizing and said reducing atmospheres, between the oxidizing and reducing atmospheres, and **in that** gaseous H_2O is caused to be present in a downstream section (211) of the annealing device through which the metal material is conveyed before reaching the reduction device.

2. Method according to claim 1, **characterized in that** the reducing atmosphere is caused to comprise H_2, **in that** the atmosphere of the reduction device (205b) is circulated counter-currently with respect to the travel direction (D) of the metal material (210), so that H_2 from the reduction device reaches the said downstream section (211) of the annealing device (205a), and **in that** the water vapour is caused to be present in the said downstream section by supplying O_2 to the downstream section, which O_2 is caused to react with the H_2 from the reduction device.

3. Method according to claim 2, **characterized in that** the O_2 is supplied to the said downstream section (211) in the form of a gas containing at least 85% O_2.

4. Method according to claim 3, **characterized in that** the O_2 is supplied to the said downstream section (211) in the form of a gas containing at least 95% O_2.

5. Method according to any one of the preceding claims, **characterized in that** water vapour is supplied directly to the said downstream section (211) of the annealing device (205a).

6. Method according to any one of the preceding claims, **characterized in that** the annealing device (205a) and the reduction device (205b) are part of the same furnace chamber, through which furnace chamber gases are circulated counter-currently in relation to the travel direction of the metal material (D) from the reduction device into the annealing device.

7. Method according to any one of the preceding claims, **characterized in that** the reducing atmosphere is heated to between 700 and 1300°C.

8. Method according to claim 7, **characterized in that** the reducing atmosphere is heated using induction heaters, direct electrical heaters or radiation tubes (212) arranged in the reduction device (205b).

9. Method according to any one of the preceding claims, **characterized in that** the dew point of the reducing atmosphere is - 20°C or less.

10. Method according to any one of the preceding claims, **characterized in that** the oxidizing atmosphere is heated using at least one burner (213) with an open flame.

11. Method according to any one of the preceding claims, **characterized in that** the metal material (210) is conveyed, after the reduction device (210b), to a cooling device (205c), without being subjected to any atmosphere apart from the said reducing atmosphere and another reducing atmosphere present in the cooling device, and **in that** the temperature of the metal material is brought to below 400°C in the cooling device.

12. Method according to any one of the preceding claims, characterized i n that the metal material (210) is a stainless or high alloyed steel, or a copper alloy.

13. Method according to claim 12, **characterized in that** the metal material (210) is a stainless steel comprising Cr.

Fig. 1

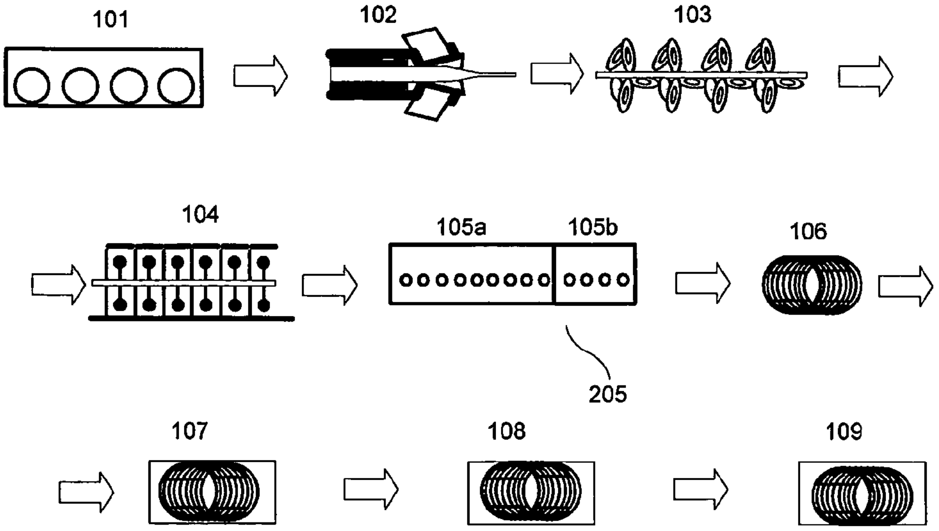

101
102
103
104
105a
105b
106
205
107
108
109

Fig. 2

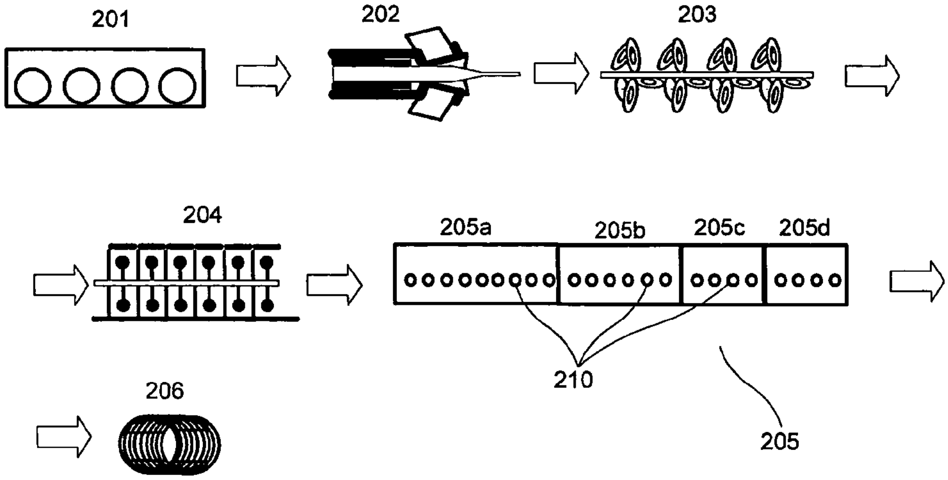

201
202
203
204
205a
205b
205c
205d
210
205
206

Fig. 3

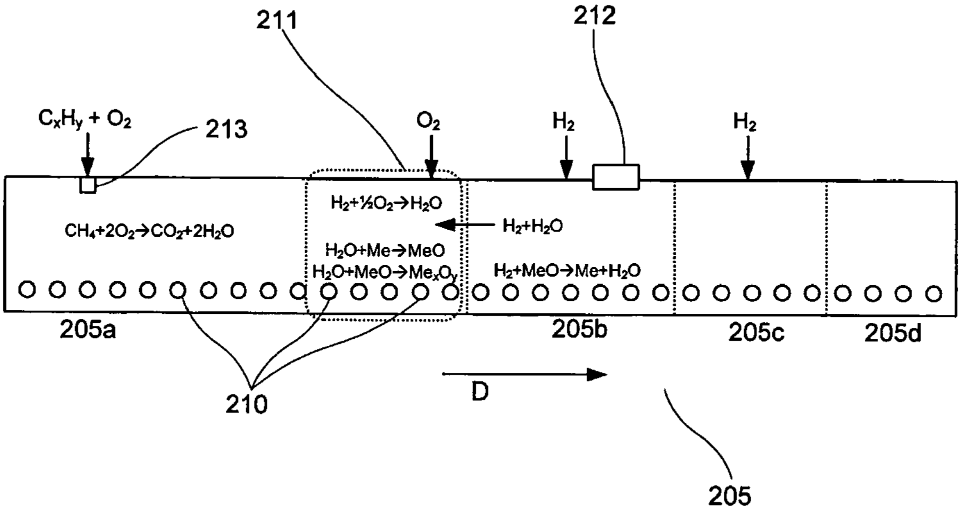

211
212
$C_xH_y + O_2$
213
O_2
H_2
H_2
$H_2+½O_2 \rightarrow H_2O$
$CH_4+2O_2 \rightarrow CO_2+2H_2O$
H_2+H_2O
$H_2O+Me \rightarrow MeO$
$H_2O+MeO \rightarrow Me_xO_y$
$H_2+MeO \rightarrow Me+H_2O$
205a
205b
205c
205d
210
D
205

Fig. 4

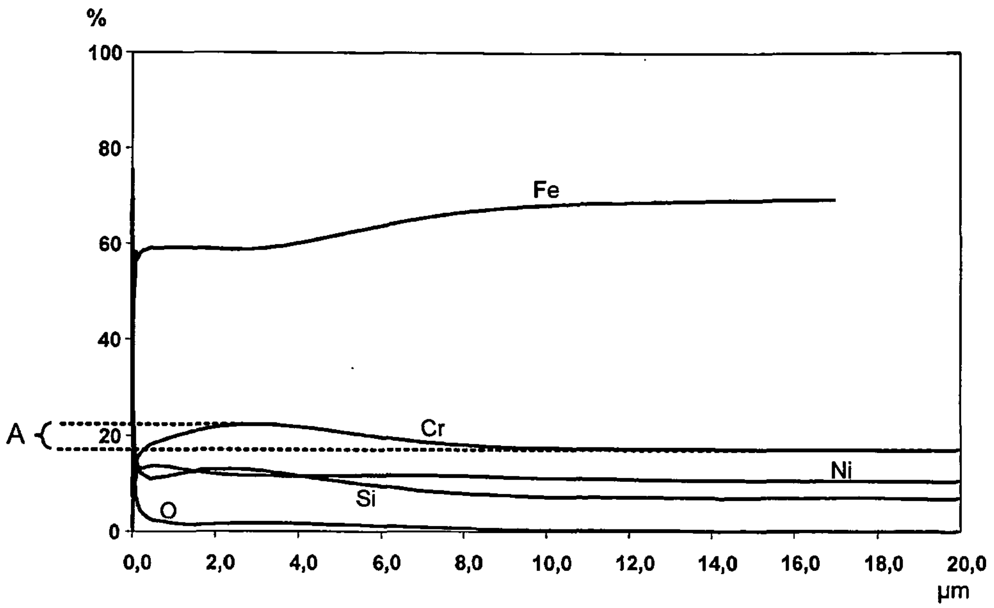
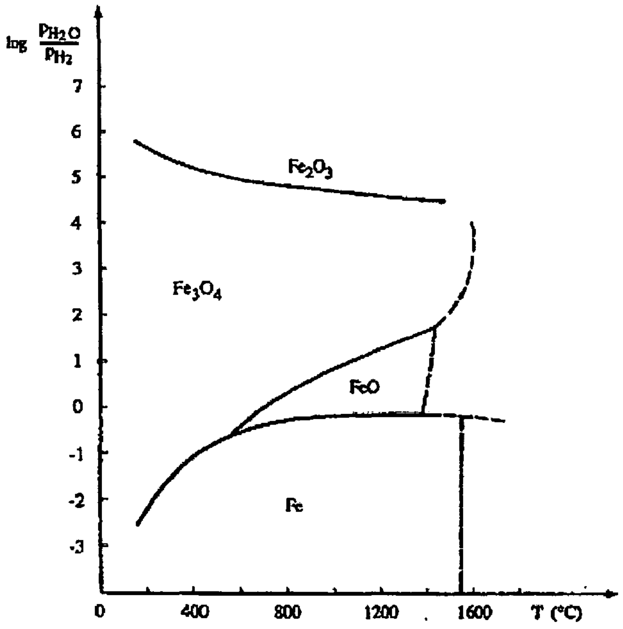

%
100
80
60
40
20
0
A
Fe
Cr
Ni
Si
O
0,0
2,0
4,0
6,0
8,0
10,0
12,0
14,0
16,0
18,0
20,0
µm

Fig. 5


$\log \frac{p_{H_2O}}{p_{H_2}}$
7
6
5
4
3
2
1
0
-1
-2
-3
Fe_2O_3
Fe_3O_4
FeO
Fe
0
400
800
1200
1600
T (°C)

Europäisches
Patentamt
European
Patent Office
Office européen
des brevets

EUROPEAN SEARCH REPORT

Application Number
EP 12 00 5250

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	DE 10 2009 018683 A1 (SMS SIEMAG AG [DE]) 28 October 2010 (2010-10-28) * paragraph [0034] - paragraph [0036] * * claims 1-18; figures 1,2 * -----	1,3,4,7,8	INV. C21D1/76 C21D8/02 C21D9/56 C23C2/02
X	DE 10 2010 037254 A1 (THYSSENKRUPP STEEL EUROPE AG [DE]) 1 March 2012 (2012-03-01) * paragraphs [0007], [0055]; claims 1-14; figure 1; table 3 * -----	1,3,4,7-13	
X	US 2010/173072 A1 (BORREL PIERRE-JEROME [FR]) 8 July 2010 (2010-07-08) * paragraphs [0006], [0011] - [0013], [0041] - [0043]; claim 12 * -----	1,3-5,8	
			TECHNICAL FIELDS SEARCHED (IPC)
			C21D C23C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	29 November 2012	Rischard, Marc

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons
....
& : member of the same patent family, corresponding document

2

EPO FORM 1503 03.82 (P04C01)

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 12 00 5250

29-11-2012

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE 102009018683 A1	28-10-2010	CN 102413954 A	11-04-2012
		DE 102009018683 A1	28-10-2010
		EP 2421664 A1	29-02-2012
		KR 20110128917 A	30-11-2011
		US 2012043049 A1	23-02-2012
		WO 2010121763 A1	28-10-2010
DE 102010037254 A1	01-03-2012	DE 102010037254 A1	01-03-2012
		WO 2012028465 A1	08-03-2012
US 2010173072 A1	08-07-2010	CN 101796203 A	04-08-2010
		EP 2188399 A1	26-05-2010
		FR 2920439 A1	06-03-2009
		JP 2010538163 A	09-12-2010
		US 2010173072 A1	08-07-2010
		WO 2009030823 A1	12-03-2009

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- WO 0204145 A **[0003]**
- EP 1935508 A **[0006]**