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(54) **MICROALLOYED STEEL FOR HEAT-FORMING HIGH-RESISTANCE AND HIGH-YIELD-STRENGTH PARTS, AND METHOD FOR PRODUCING COMPONENTS MADE OF SAID STEEL**

(57) The invention relates to a microalloyed steel for heat-forming high-strength and high-yield strength parts, and to a method for producing components made of said steel, having a specific composition of the following elements: $0.30\% \leq C \leq 0.50\%$, $0.50\% \leq Si \leq 1.50\%$, $0.50\% \leq Mn \leq 1.50\%$, $0.005\% \leq V < 0.50\%$, $0.001\% \leq Ti < 0.050\%$ which, using a method suitable for producing said steel, achieves low P content and good inclusion cleanliness. In addition, tensile strength values between 1050 and 1200 MPa are achieved using a controlled cooling process.

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Description

Object of the Invention

[0001] The present invention relates to a high-strength and high-yield strength microalloyed steel, as well as to a method for producing components made of said steel, whereby the mechanical characteristics required are achieved by means of controlled cooling.

[0002] The invention allows producing a microalloyed steel with high mechanical strength and high yield strength, in addition to responding well to machining operations, based on a given chemical composition, a specific metallurgical process and subsequent controlled cooling.

Background of the Invention

[0003] Microalloyed steel is basically classic building steel to which small amounts of alloy elements, such as V, Al, Ti, Nb, Zr, B, etc., capable of forming microprecipitates are added.

[0004] The main characteristic of microalloyed steels is based on the occurrence of microprecipitates produced during both the rolling process and the forging process. It is therefore necessary to know the formation and evolution of microprecipitates as a function of thermal cycles, hot deformations and cooling rates in order to dominate the process and produce steel with the desired mechanical properties.

[0005] One of the main applications of microalloyed steels are certain automotive engine components, such as the crankshaft, connecting rods, the rail of common-rail, etc. All these elements are components subjected to high working pressures and stresses, so it is fundamental for them to have very high tensile strength and yield strength values.

[0006] The advantage with respect to quenched and tempered steels they are replacing is based on the fact that these microalloyed steels acquire characteristics directly by means of thermomechanical treatment and subsequent controlled cooling.

[0007] The microalloyed steels of the present patent have a ferrite-perlite structure, and their final application is in heat-forming.

[0008] On the other hand, the machinability of microalloyed steel after a heat-forming process is comparable to that of quenched and tempered steel, provided that they both have similar hardness and sulfur content levels.

[0009] The main advantage derived from the use of microalloyed steels is the direct reduction of the cost of the formed components up to 10-20%, primarily due to the simplification of the manufacturing process by eliminating thermal treatment from quenching and tempering, as well as subsequent straightening operations, stress relief operations, as well as hardening cracks and controls for detecting them.

[0010] Different microalloyed steel grades are used today according to the strength to be attained in components for which they are going to be used. The characteristics are largely determined by the carbon content of the steel, which can range between 0.15% and 0.50% by weight, as well as the content of other alloying elements, such as Mn and Si, for example, which help with solid solution hardening of ferrite and other microalloying elements such as Ti, V and, in some cases, Nb as well, which form carbide and nitride microprecipitates, functioning as controllers of grain size and precipitation hardening.

[0011] The different microalloyed steel grades manufactured today range from 550 MPa to 1000 MPa in terms of strength. These values considerably depend on the thickness of the part and on the forming process and subsequent cooling to which the part is subjected.

[0012] There are different patents today related to microalloyed steels. Several examples are mentioned below.

[0013] Patent application no. CN102776439(A)2012 "Niobium microalloying Si-Mn-B series hot forming steel plate and rolling technology" describes a microalloyed steel with Nb but for a flat product with a mechanical strength between 700-900 MPa and a yield strength of 500-600 MPa.

[0014] Patent application no. CN101629268(A)2010 "Microalloying high-strength and anti-crack flat steel for automobile girder and production process thereof" describes a microalloyed steel in V producing an as-rolled product between 750-850 MPa and a yield strength between 640-700 MPa.

[0015] Patent application no. CN101307413(A)2008 "Microalloying steel for ultra-high-strength sucker rod" describes a microalloyed steel with Nb, Ti and V for rods, with a tensile strength greater than 965 MPa.

[0016] Therefore, there is no microalloyed steel in the state of the art with a tensile strength exceeding 1000 MPa.

Description of the Invention

[0017] A first aspect of the present invention relates to microalloyed steel for forming high-strength and high-yield strength parts as defined in Claim 1. The steel of the invention consists of a ferrite-perlite structure with mechanical characteristics in which the tensile strength is 1050-1200 MPa, depending on the diameter of the bar and the yield

strength is greater than 750 MPa.

[0018] The invention allows producing a microalloyed steel from a novel chemical composition and a given metallurgical process, having high mechanical strength while at the same time high yield strength, which is fundamental for all automotive components.

[0019] On the other hand, in addition to the chemical composition, a second aspect of the invention relates to a method for producing microalloyed steel like the one described above, as defined in Claim 6, as well as to a method for producing components according to the steel described above, as defined in Claim 7. The thermomechanical treatment to which the component formed with the steel in question is subjected has a very important influence on the microstructure, and therefore on the mechanical characteristics of the end component, i.e., the steel with the initial chemical composition must be formed under given conditions and be subjected to controlled cooling under certain conditions in order to achieve the optimized mechanical characteristics of the end component.

[0020] In order to assure good mechanical characteristics which in turn entail a long fatigue life, a specific deoxidation and inclusions separation method in given special conditions must be applied during the manufacturing process for producing this steel.

[0021] A synergistic effect has been found between a novel combination of chemical elements and a method of controlled cooling to obtain the characteristics required for said steel.

[0022] In turn, since most of the automotive components for which this steel has been designed require significant machining operations after the forging process, the chemical composition of this steel is designed so that its post-forming process machinability is comparable to or even better than that of classic quenched and tempered steel when they both have similar hardness and sulfur content levels.

[0023] The research that was conducted resulted in a new SiMnV alloyed steel grade, comprising the following chemical composition in percentage by weight:

$0.30\% \leq C \leq 0.50\%$
$0.50\% \leq Si \leq 1.50\%$
$0.50\% \leq Mn \leq 1.50\%$
$0.05\% \leq V \leq 0.50\%$
$0.001\ \% \leq Ti \leq 0.050\%$

[0024] Furthermore, the possibility that the steel of the invention may possibly comprise at least one of the following elements is contemplated: up to 0.15% of Bi, up to 0.20% of Pb, up to 0.02% of Te, up to 0.04% of Se, the remaining elements being impurities resulting from the manufacturing process.

[0025] These alloy elements are used in microalloyed steels to improve the tensile strength and other characteristics that allow the use thereof in the discussed applications.

[0026] Each of the alloy elements, in the proportions indicated above, has an influence on given parameters and properties of the steel that is finally produced.

[0027] Carbon is an essential element for obtaining high strength and hardness, as well as a long fatigue life. In the microalloyed steels, carbon tends to form carbides, hardening and providing strength to said steels.

[0028] In addition to being a strong deoxidizer, silicon provides solid solution hardening as it dissolves into the ferrite matrix.

[0029] Manganese prevents the detrimental effect of sulfur, combining with it to form MnS and thereby improving machinability. On the other hand, like silicon, manganese dissolves in the ferrite crystalline network, replacing the iron atoms and causing solid solution hardening.

[0030] Vanadium is a microalloying element that contributes to refining the grain size and when it combines with carbon, it forms vanadium carbides, which bring about intense precipitation hardening. Vanadium precipitates are hydrogen nucleators, such that in corrosive environments they fix it and improve hydrogen-induced delayed fracture resistance. However, with very high vanadium contents the precipitates coalesce and their effect can become detrimental. Therefore, the optimal vanadium content is between 0.05% and 0.50%.

[0031] Furthermore, it is contemplated that the steel proposed by the invention may additionally comprise at least one of the following elements, or a combination thereof, in percentage by weight:

$P \leq 0.015\%$
$S \leq 0.10\%$
$Cr \leq 0.50\%$
$Ni \leq 0.50\%$
$Mo \leq 0.10\%$
$Cu \leq 0.25\%$
$0.001\ \% \leq Al \leq 0.050\%$

0.001 %≤ Nb ≤ 0.050%
0.004% ≤ N ≤ 0.020%

[0032] Phosphorus hardens the steel and segregates at the austenite grain boundaries, drastically reducing the toughness of the steel. Furthermore, it favors hydrogen embrittlement and delayed fracture. In order to limit its adverse effect, the phosphorus content is limited to less than 0.015%.

[0033] Sulfur embrittles steel similarly to phosphorus. Despite the fact that this effect is counteracted by combining with manganese, manganese sulfides form inclusions which deform longitudinally in the forging or rolling direction and considerably deteriorate transverse mechanical properties and fatigue behavior. However, sulfur must be added in small amounts because it brings about microalloyed steel machinability improvements, hence the content thereof being limited to 0.10%.

[0034] Chromium is an essential element for assuring steel quenchability; however, since a ferrite-perlite structure is desired for the microalloyed steel of the invention, chromium is an element that must be controlled, hence it is limited to a maximum of 0.50%.

[0035] Nickel is an element which, at high concentrations, inhibits ferrite formation and furthermore favors quenchability; hence, like chromium, nickel is an element that must be controlled in microalloyed steels. For that reason, it must be limited to a maximum of 0.50%

[0036] Molybdenum has an effect which greatly favors quenchability, just like chromium and even more than nickel; hence, for a microalloyed steel with a ferrite-perlite structure it is limited to a maximum of 0.10%.

[0037] The addition of copper prevents steel decarburization and improves corrosion resistance in a manner similar to nickel, inhibiting the growth of corrosion pits. However, a high copper content impairs hot ductility of the steel such that the upper limit of copper is set at 0.25%.

[0038] Aluminum is an element that acts like a strong deoxidizer during the steel manufacturing process. Aluminum forms aluminum nitrides which contribute to controlling austenite grain size during heating prior to heat-forming processes. Nevertheless, it forms very hard oxides that are highly detrimental for fatigue life, such that the upper limit thereof is set at less than 0.050%.

[0039] Niobium is a microalloying element having effects similar to those of vanadium on grain size control and on precipitation hardening of the steel, such that it contributes to increasing the mechanical strength and to improving toughness. Furthermore, niobium precipitates fix the hydrogen attacking the steel in corrosive environments, improving the delayed fracture resistance. At more than 0.050%, nevertheless, the precipitates swell, which is detrimental for the mechanical properties, in addition to increasing the risk of the occurrence of bainites. The optimal niobium content is set between 0.001% and 0.050%.

[0040] Nitrogen combines with Ti, Nb, Al and V to form nitrides, the precipitation temperatures of which depend on the respective content of the different elements and on constant features. With a suitable size, those nitrides exert a pinning effect on the austenite grain by controlling its size at a high temperature and preventing coalescence and growth thereof. However, if the nitrogen or microalloying element content is very high, precipitation occurs at a high temperature and the precipitates swell, being rendered ineffective for controlling grain and detrimental for the fatigue life. As a result, the nitrogen content in the steel is limited to 0.004% to 0.020%.

[0041] A preferred composition of the starting steel part in percentage by weight is the following:

0.35% ≤ C ≤ 0.48%
0.55% ≤ Si ≤ 1.40%
0.55% ≤ Mn ≤ 1.40%
0.05% ≤ V ≤ 0.40%
0.005% ≤ Ti ≤ 0.040%

[0042] For this preferred composition, the steel can additionally comprise at least one of the following elements, or a combination thereof, by weight:

P ≤ 0.015%
S ≤ 0.10%
Cr ≤ 0.50%
Ni ≤ 0.50%
Mo ≤ 0.10%
Cu ≤ 0.25%
0.001 % ≤ Al ≤ 0.050%
0.001 % ≤ Nb ≤ 0.050%
0.004% ≤ N ≤ 0.020%

[0043] Therefore, after various experiments a rigorous method for producing steel according to the following steps has been developed:

- Rigorously controlling the raw materials from the furnace.
- Performing an oxidation period in an electric furnace, which is important for dephosphorization of the steel, prior to foamed slag.
- Once foamed slag has ended, deslagging is performed until rendering the furnace virtually slag-free, the objective being a presence of phosphorus in this step less than 0.007% by weight.
- Tipping until overturning with standard temperature and parts per million (ppm) of oxygen, making sure that slag does not go from the furnace to the ladle.
- Generating a prolonged vacuum, a vacuum below 1 mbar being considered the vacuum time.
- Ending the vacuum treatment with sufficient temperature to perform an inclusion separation process after same lasting at least fifteen minutes, without performing additions or heating of any type.
- Finally, a meticulous casting process must be followed with special protection of the liquid steel stream.
- If the solidification process is in continuous casting, the casting speed, cooling and stirring conditions will be adjusted for producing a microstructure with homogenous solidification.
- Providing a suitable design of the secondary cooling, as well as a slow tertiary cooling, in order to prevent thermo-mechanical stresses that may result in the occurrence of cracks.
- Reaching the straightening at a temperature above the temperatures at which hot ductility decreases for these steels.

[0044] This entire method of manufacturing the steel allows achieving the desired sulfur levels and phosphorus levels below 0.015% by weight, in addition to a low inclusion level.

[0045] The CCT (continuous cooling transformation) diagrams allow knowing the cooling rates suitable for obtaining a ferrite-perlite microstructure in the steel according to the invention.

[0046] The solidification products are later transformed in heat conditions by means of a process that consists of heating at a temperature between 900-1300°C and a series of consecutive deformations by means of hot forging or rolling until producing an intermediate product having a suitable section, shape and microstructure.

[0047] After various experimental tests, it was found that after the process of manufacturing the steel proposed by the invention, with the chemical composition indicated above and adjusting the cooling rates after the forging or rolling process, a steel having a ferrite-perlite structure, with a tensile strength between 1050 and 1200 MPa, depending on the section of the bar or component, is achieved.

[0048] To produce a component made of the steel previously produced having the mentioned features, the invention contemplates the possibility of carrying out a method whereby said steel part can be produced. Said possibility comprises, after producing the steel, the following steps:

- manufacturing a component made of said steel,
- performing controlled cooling of the component immediately after heat-forming,
- machining the component with its final geometry.

[0049] Therefore, according to an embodiment the method for producing parts made of said steel comprises a heat-forming process, with prior heating at a temperature between 900-1300°C, which allows providing the steel with sufficient hot ductility, in order to give the part of steel a shape similar to that of the end component. After shaping, the part is subjected to controlled cooling, which will allow achieving the desired mechanical characteristics with a 100% ferrite-perlite structure.

[0050] It is subsequently contemplated that said embodiment of the method for manufacturing the microalloyed steel part comprises a machining process machining to obtain the final geometry of the component, hence in order to improve the response of the steel with respect to machinability, the steel can possibly have elements such as sulfur and other elements for improving machinability.

[0051] Therefore, it is contemplated that an embodiment of the method for producing steel parts comprises the following steps:

- Manufacturing the steel of the invention described above, in which the selected steel comprises the general composition or the preferred composition defined above.
- Process of rolling the steel in question.
- Manufacturing a part made of said steel by means of a heat-forming process.
- Controlled cooling of the part after heat-forming.
- Machining operations on the formed part.

Description of the Drawings

[0052] To complement the description that is being made and for the purpose of helping to better understand the features of the invention according to a preferred practical embodiment thereof, a set of drawings is attached as an integral part of said description, in which the following is depicted with an illustrative and non-limiting character:

Figure 1 shows a table, divided into Figures 1 a and 1 b, comprising photographs of the microstructures obtained after heat-forming for the same part in the samples of steels A-G defined in Table 1.
Figure 2 shows photographs of the microstructures in which details of the bainites found in castings B, C, D and E can be seen.

Embodiments of the Invention

Example 1

[0053] By way of example, the tests conducted with samples of steels with other compositions different from the chemical composition of the steel of the invention are described below. Said samples are steels A-G, where steel H is the steel of the invention. Table 1 shows the chemical compositions in percentage by weight, the rest being iron and impurities:

Table 1

	C	Mn	Si	P	S	Cr	Ni	Mo	V	Cu	Al	Ti	N*
A	0.36	1.05	0.72	0.009	0.023	0.12	0.09	0.020	0.26	0.13	0.019	0.025	152
B	0.38	1.37	0.72	0.009	0.069	0.15	0.14	0.032	0.25	0.21	0.010	0.009	136
C	0.37	1.39	0.95	0.012	0.073	0.13	0.14	0.034	0.26	0.21	0.008	0.009	207
D	0.40	1.40	1.28	0.010	0.060	0.19	0.13	0.033	0.26	0.20	0.004	0.006	95
E	0.40	1.42	1.51	0.010	0.062	0.18	0.13	0.033	0.25	0.21	0.004	0.006	99
F	0.40	1.16	1.06	0.007	0.063	0.15	0.12	0.028	0.25	0.07	0.009	0.014	133
G	0.44	1.40	0.40	0.011	0.070	0.21	0.06	0.020	0.12	0.10	0.017	0.016	137
H	0.44	1.21	0.91	0.008	0.025	0.09	0.08	0.012	0.26	.010	0.011	0.013	162
(*) ppm													

[0054] Table 2 shows the values of the mechanical characteristics obtained for one and the same component already formed with all the castings of Table 1.

Table 2

	Yield strength (MPa)	Tensile strength (MPa)	Elongation (%)	Reduction (%)
A	698	954	18	48
B	824	1102	13	25
C	779	1056	9	18
D	880	1140	10	38
E	887	1141	8	32
F	740	1016	18	40
G	648	956	21	41
H	804	1118	15	35

[0055] It can be seen that steels B-C-D and E have exceeded a strength of 1050 MPa and yield strength of 750 MPa; however, the microstructure of these steels after heat-forming have shown traces of bainites.

[0056] The following table shows the different percentages of phases found in the different components with the castings of Table 1.

Table 3

	Ferrite (%)	Perlite (%)	Bainite (%)
A	40	60	0
B	10	65	25
C	15	75	10
D	20	75	5
E	15	80	5
F	40	60	0
G	35	65	0
H	35	65	0

[0057] Figure 1 shows the photographs of the microstructures produced after heat-forming for one and the same part.

[0058] Figure 2 shows the details of the bainites found in castings B, C, D and E.

[0059] As shown in Table 2, steels A and G do not reach a strength of 1000 MPa. Steel A has a low percentage of carbon and manganese, such that it does not reach the strength of 1000 MPa or yield strength of 700 MPa. In turn, even though steel G has a higher percentage of carbon and manganese than steel A does, it has a low percentage of silicon, as well as a low percentage of vanadium, such that precipitation hardening is less than in the case of steel A.

[0060] Steel F has a tensile strength greater than 1000 MPa and a yield strength of 700 MPa, somewhat greater than steels A and G. However, the mechanical characteristics object of the present patent have not been achieved due to the percentage of carbon at a level that is somewhat below the suitable level.

[0061] The compositions of steels B and C were designed as a function of the composition of steel A, but increasing the percentages of manganese in the case of steel B and manganese and silicon in the case of steel C. Therefore, even though strengths exceeding 1050 MPa and yield strengths around 800 MPa were achieved, the percentages of bainite obtained were not acceptable for microalloyed steel with a ferrite-perlite microstructure.

[0062] The chemical compositions of steels D and E were subsequently designed, in which in addition to the percentage of carbon, the percentage of manganese of casting B was maintained and the percentages of silicon were increased. However, despite obtaining good mechanical characteristics with strengths greater than 1100 MPa and yield strengths greater than 800 MPa, residual percentages of bainite continued to show up in the different components.

[0063] However, for steel H, which has a chemical composition within the limits object of the invention, i.e., the steel proposed by the invention, it has been found that a strength of 1100 MPa can be achieved for bar-shaped parts 30 mm in diameter.

[0064] The invention has been described according to several preferred embodiments thereof, but for the person skilled in the art it will be obvious that multiple variations can be introduced in said preferred embodiments without exceeding the object of the claimed invention.

Claims

1. Microalloyed steel with high tensile strength and high yield strength, **characterized in that** it comprises the following elements in percentage by weight:

   $0.30\% \leq C \leq 0.50\%$
   $0.50\% \leq Si \leq 1.50\%$
   $0.50\% \leq Mn \leq 1.50\%$
   $0.05\% \leq V \leq 0.50\%$
   $0.001\ \% \leq Ti \leq 0.050\%$.

2. Microalloyed steel according to the claim 1, comprising at least one of the following elements in percentage by weight:

   $P \leq 0.015\%$

S ≤ 0.10%
Cr ≤ 0.50%
Ni ≤ 0.50%
Mo ≤ 0.10%
Cu ≤ 0.25%
0.001 % ≤ Al ≤ 0.050%
0.001 %≤ Nb ≤ 0.050%
0.005% ≤ N ≤ 0.020%.

3. Microalloyed steel according to any of the preceding claims, comprising the following elements in percentage by weight:

0.35% ≤ C ≤ 0.48%
0.55% ≤ Si ≤ 1.40%
0.55% ≤ Mn ≤ 1.40%
0.05% ≤ V ≤ 0.40%
0.005% ≤ Ti ≤ 0.040%.

4. Microalloyed steel according to claim 3, comprising at least one of the following elements in percentage by weight:

P ≤ 0.015%
S ≤ 0.10%
Cr ≤ 0.50%
Ni ≤ 0.50%
Mo ≤ 0.10%
Cu ≤ 0.25%
0.001 % ≤ Al ≤ 0.050%
0.001 %≤ Nb ≤ 0.050%
0.004% ≤ N ≤ 0.020%.

5. Microalloyed steel according to any of the preceding claims, having a strength between 1050 and 1200 MPa and a yield strength greater than 750 MPa.

6. Method for producing a microalloyed steel according to any of claims 1 to 5, **characterized in that** it comprises the following steps:

- controlling the raw materials of the furnace,
- performing an oxidation period in an electric furnace, prior to foamed slag,
- deslagging until leaving a presence of phosphorus less than 0.007% by weight,
- tipping until overturning with standard temperature and parts per million (ppm) of oxygen, making sure that slag does not go from the furnace to the ladle,
- generating a prolonged vacuum, a vacuum below 1 mbar being considered the vacuum time,
- ending the vacuum treatment with sufficient temperature to perform an inclusion separation process after same lasting at least fifteen minutes, without performing additions or heating of any type,
- in continuous casting, adjusting the casting speed, cooling and stirring conditions for producing a microstructure with homogenous solidification, and in casting in ingots, protecting the casting stream,
- providing a suitable design of the secondary cooling, as well as a slow tertiary cooling, in order to prevent thermomechanical stresses that may result in the occurrence of cracks,
- reaching the straightening at a temperature above the temperatures at which hot ductility decreases for these steels.

7. Method for producing components of microalloyed steel according to claim 6, wherein after producing the steel, the method comprises the following steps:

- manufacturing a component made of said steel,
- performing controlled cooling of the component immediately after heat-forming, and
- machining the component with its final geometry.

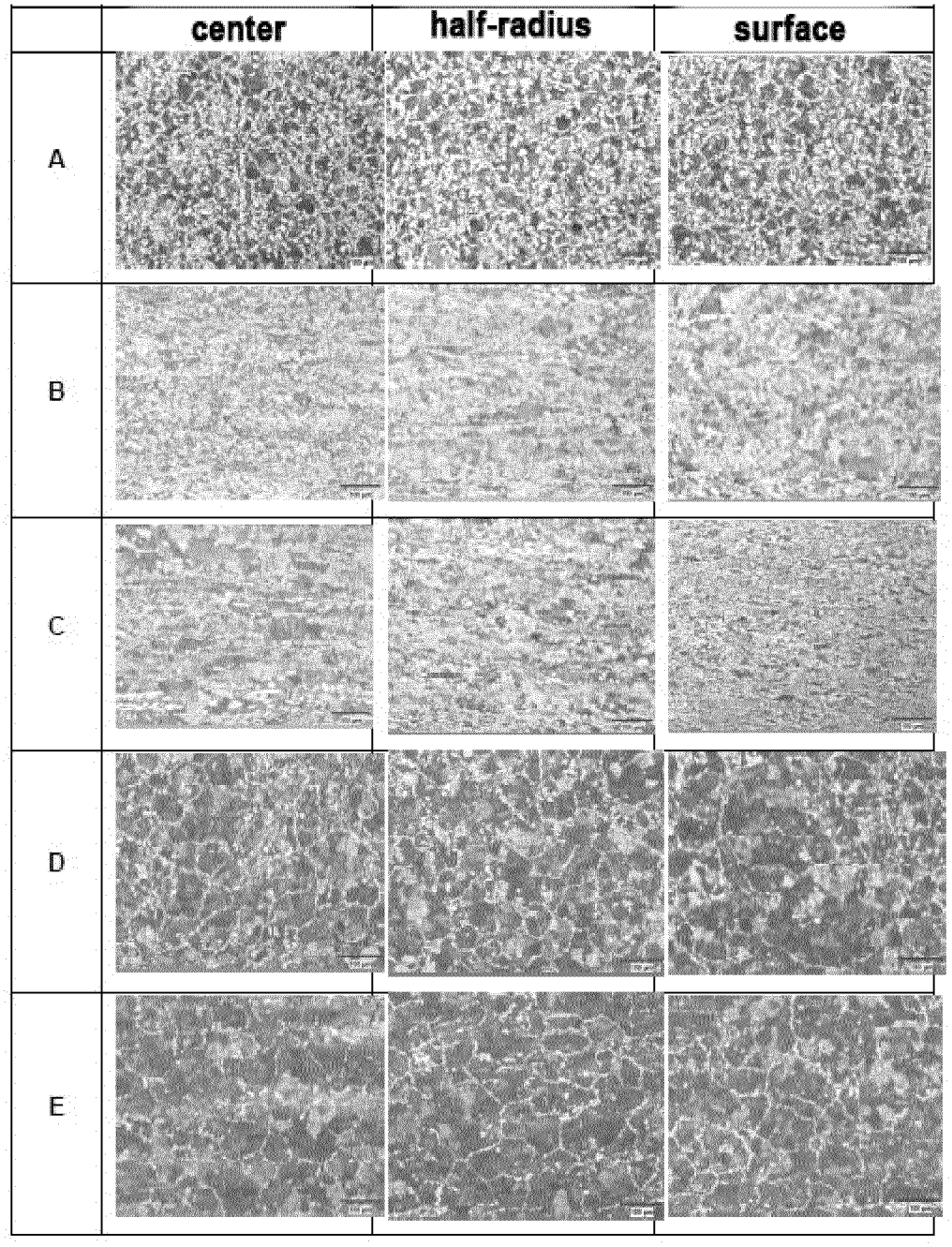


FIG. 1a

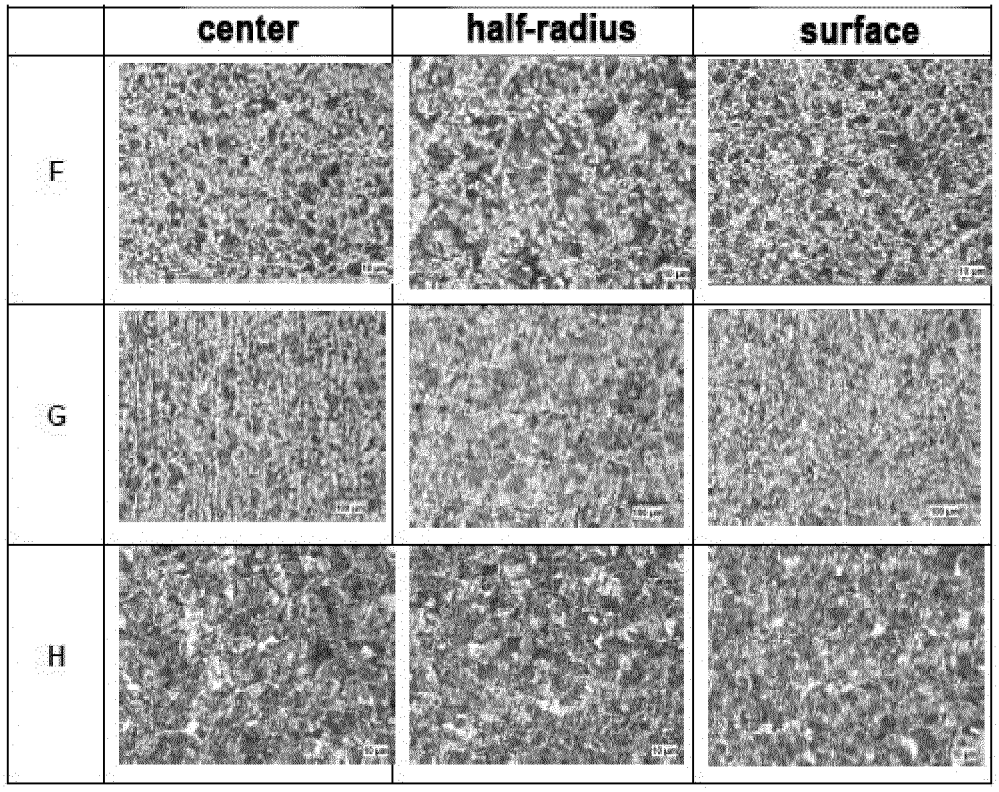


FIG 1b

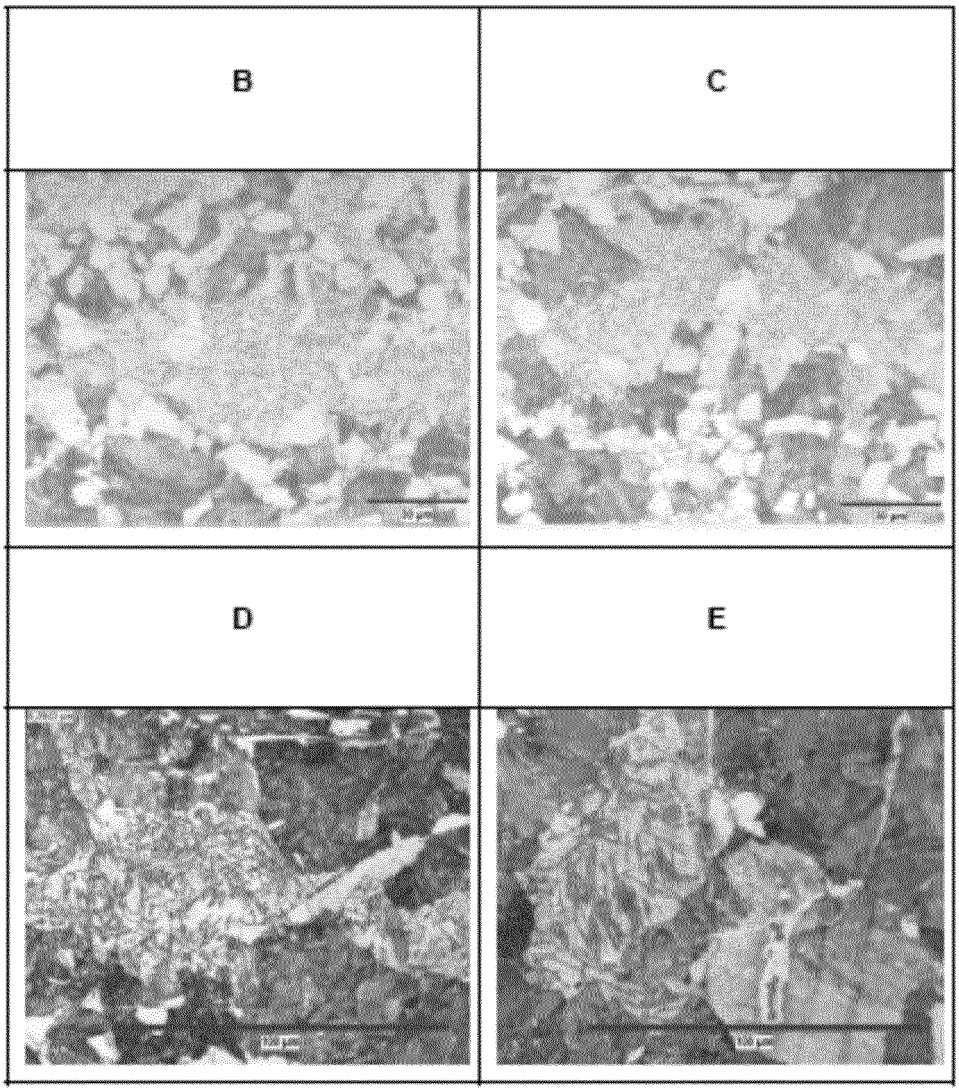


FIG 2

INTERNATIONAL SEARCH REPORT

International application No.
PCT/ES2014/070558

A. CLASSIFICATION OF SUBJECT MATTER

See extra sheet

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C22C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

INVENES, WPI, EPODOC, XPESP, TXTEP1, TXTGB1, TXTUS2, TXTUS3, TXTUS4

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 2524970 A1 (THYSSENKRUPP STEEL EUROPE AG) 21/11/2012, paragraph [18];	1-7
A	ES 2302935T T3 (CDP BHARAT FORGE GMBH) 01/08/2008, page 3, lines 6 - 35;	1-7
A	FR 2833617 A1 (USINOR) 20/06/2003, claim 1,	1-7
A	EP 1568792 A1 (JFE STEEL CORP) 31/08/2005, claim 1,	1-7

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
19/02/2015	**(20/02/2015)**
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/ES2014/070558

Patent document cited in the search report	Publication date	Patent family member(s)	Publication date
EP2524970 A1	21.11.2012	US2014322559 A1	30.10.2014
		JP2014518945 A	07.08.2014
		KR20140024903 A	03.03.2014
		EP2710158 A1	26.03.2014
		CN103597100 A	19.02.2014
		WO2012156428 A1	22.11.2012
ES2302935T T3	01.08.2008	US2006102257 A1	18.05.2006
		MXPA05003228 A	12.09.2005
		SI1546426T T1	31.10.2008
		JP2006500474 A	05.01.2006
		WO2004031428 A1	15.04.2004
		EP1546426 A1	29.06.2005
		EP1546426 B1	09.04.2008
		DK1546426T T3	16.06.2008
		CN1685074 A	19.10.2005
		CN100374602C C	12.03.2008
		BR0314708 A	26.07.2005
		BR0314708 B1	19.08.2014
		AU2003267053 A1	23.04.2004
		AT391795T T	15.04.2008
		EP1408131 A1	14.04.2004
FR2833617 A1	20.06.2003	EP1319726 A1	18.06.2003
EP1568792 A1	31.08.2005	CN1661126 A	31.08.2005
		CN100354436C C	12.12.2007
		RU2360013 C2	20.08.2006
		RU2005104964 A	20.08.2006
		US2005183798 A1	25.08.2005
		US7879287 B2	01.02.2011
		KR20050086375 A	30.08.2005
		KR100673425B B1	24.01.2007
		CA2491307 A1	24.08.2005
		CA2491307 C	27.03.2012
		JP2005240051 A	08.09.2005
		JP4305216B B2	29.07.2009

Form PCT/ISA/210 (patent family annex) (July 2009)

INTERNATIONAL SEARCH REPORT

International application No.

PCT/ES2014/070558

CLASSIFICATION OF SUBJECT MATTER

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C22C38/04 (2006.01)
C22C38/12 (2006.01)
C22C38/14 (2006.01)

Form PCT/ISA/210 (extra sheet) (July 2009)

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- CN 102776439 A **[0013]**
- CN 101629268 A **[0014]**
- CN 2010 A **[0014]**
- CN 101307413 A **[0015]**