

(19)



(11)

EP 3 280 826 B1

(12)

EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention of the grant of the patent:

18.03.2020 Bulletin 2020/12

(51) Int Cl.:

C21D 6/00 <small>(2006.01)</small>	C21D 8/10 <small>(2006.01)</small>
B21B 21/00 <small>(2006.01)</small>	B21C 1/22 <small>(2006.01)</small>
C22C 38/42 <small>(2006.01)</small>	C22C 38/44 <small>(2006.01)</small>
C22C 38/02 <small>(2006.01)</small>	C22C 38/04 <small>(2006.01)</small>
C22C 38/58 <small>(2006.01)</small>	C22C 38/00 <small>(2006.01)</small>

(21) Application number: **16718275.7**

(22) Date of filing: **08.04.2016**

(86) International application number:
PCT/EP2016/057831

(87) International publication number:
WO 2016/162525 (13.10.2016 Gazette 2016/41)

(54) A METHOD OF PRODUCING A TUBE OF A DUPLEX STAINLESS STEEL

VERFAHREN ZUR HERSTELLUNG EINES ROHRS EINES ROSTFREIEN DUPLEXSTAHLS

PROCÉDÉ DE PRODUCTION D'UN TUBE EN ACIER INOXYDABLE DUPLEX

(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

(30) Priority: **10.04.2015 EP 15163187**

(43) Date of publication of application:
14.02.2018 Bulletin 2018/07

(73) Proprietor: **Sandvik Intellectual Property AB**
811 81 Sandviken (SE)

(72) Inventors:
• **PONSILUOMA, Jari**
811 62 Sandviken (SE)
• **HINDRUM, Maria**
803 24 Gävle (SE)
• **EIDHAGEN, Josefin**
811 32 Sandviken (SE)

- **PERSSON, Katarina**
803 02 Gävle (SE)
- **JONES, Russell P.**
Clarks Summit, Pennsylvania 18411 (US)
- **LARSSON, Åsa**
806 35 Gävle (SE)

(74) Representative: **Sandvik**
Sandvik Intellectual Property AB
811 81 Sandviken (SE)

(56) References cited:
EP-A2- 2 038 445 **WO-A1-2010/082395**
WO-A2-96/39543 **JP-A- S63 255 322**
JP-A- 2012 139 693 **US-A1- 2011 067 475**

- **Pilger Mill Technologies: "What is Pilgering", , 19 December 2011 (2011-12-19), XP002747327, Retrieved from the Internet: URL:http://pilgermilltechnologies.com/What_is_Pilgering.html [retrieved on 2015-10-19]**

EP 3 280 826 B1

Note: Within nine months of the publication of the mention of the grant of the European patent in the European Patent Bulletin, any person may give notice to the European Patent Office of opposition to that patent, in accordance with the Implementing Regulations. Notice of opposition shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

Description

TECHNICAL FIELD

5 **[0001]** The present disclosure relates to a method of producing a tube of a duplex stainless steel, in particular a duplex stainless steel suitable for use in fuel injection systems for injection of fuel into the combustion chamber of a combustion engine.

BACKGROUND

10 **[0002]** In connection to the design of Gasoline Direct Injection (GDI) systems for the automotive industry, it has been suggested to use duplex stainless steel for the rails used for conducting fuel to be injected into the combustion chamber of a combustion engine.

15 **[0003]** The requirements on a tube to be used as a GDI-rail are several, and must be considered when designing the duplex stainless steel to be used in such an application. It is thus of importance to select a chemical composition of the duplex stainless steel that, in combination with a properly chosen tube manufacturing process, results in a predetermined austenite/ferrite ratio, a requested corrosion resistance (resistance against general corrosion as well as against pitting corrosion), a microstructure essentially free from intermetallic phases, in particular sigma phase and chromium nitrides, a predetermined impact toughness, a predetermined tensile strength and a predetermined fatigue strength. Furthermore, the mechanical properties of the duplex steel should be such that the obtained tube will present a predetermined burst pressure, i.e. internal pressure until failure, which is high enough for the envisaged application, also when the wall thickness of the tube is relatively small, thereby enabling a GDI-rail that requires less space and weight. The corrosion and fatigue properties should guarantee the endurance of the tube over time.

20 **[0004]** Designing of a duplex stainless steel and the process of producing a tube thereof assumed to meet the requirements of a GDI-rail is therefore a complex task. The selected chemical composition and the production process parameters must be tuned with regard to each other. Accordingly, once a nominal chemical composition has been decided for the duplex stainless steel, the production process parameters must also be selected with regard thereto. The chemical composition of the duplex stainless steel should also promote a cost efficient production process. In other words, the chemical composition should not be such that it will require excessively complicated, energy-consuming or time-consuming production steps. A such example is given in JP S 63255322.

25 **[0005]** The aspect of the present disclosure is to present a method of producing a tube of a duplex stainless steel that enables the production of a tube of said duplex stainless steel presenting properties making the tube suitable to applications in which there are high requirements on corrosion resistance (resistance against general corrosion as well as against pitting corrosion), a predetermined impact toughness, a predetermined tensile strength and a predetermined fatigue strength.

30 **[0006]** One such application is a GDI-rail for conducting fuel to be injected into the combustion chamber of a combustion engine. The duplex stainless steel of said tube should present a microstructure essentially free from intermetallic phases, in particular sigma phase and chromium nitrides. The chemical composition of the duplex stainless steel shall enable cost-efficient production of a tube thereof in terms of promoting the use of cost-efficient process steps.

SUMMARY

35 **[0007]** The aspects mentioned above are achieved by the present disclosure which provides a method of producing a tube of duplex stainless steel as of claim 1.

40 **[0008]** Thus, it has been found that to reach optimal material properties, the annealing temperature, the annealing time and the annealing atmosphere. It has been found that the annealing temperature should be in the range of from 950 to 1060°C and the atmosphere should comprise a gas mixture of 1-6 vol% nitrogen and the remainder is selected from H₂ or an inert gas and the annealing should be performed in a time period of from 0.3-10 minutes

45 **[0009]** If lower annealing temperatures are used, there is a risk of forming un-wanted precipitates, such as intermetallic phases. Additionally, the recrystallization will be slower and therefore an increased soaking time will be required for completing the recrystallization, thus having a negative impact on productivity.

50 **[0010]** In principal, the upper temperature limit for the annealing step is set by the temperature at which the duplex stainless steel will start to melt. However, there are also practical reasons for why the annealing temperature shall be further restricted. At temperatures higher than the provided interval, the duplex stainless steel will become softer, which will increase the risk of damages during the annealing step. Also, at high temperatures, the grain growth will increase making it more difficult to obtain a good process and grain size control.

55 **[0011]** It is also very important to use an annealing temperature which will balance the phase fraction, a too low temperature will cause too low ferrite content and a too high temperature will provide too high ferrite content. The

temperature of the annealing step will also influence the chemical composition of the ferrite and the austenite phase, so the annealing temperature needs to be balanced together with the chemical composition to ensure that both these phases will have good corrosion resistance.

[0012] The time period for which the tube is subjected to the annealing temperature should be between 0.3 to 10 minutes, such as 0.3 to 5 minutes, such as 0.3 to 2.5 -minutes. This time period needs to be long enough to ensure complete recrystallization. However, if said time period is too long, the obtained tube will have a coarse structure which will have a negative impact on the mechanical properties. The larger the thickness of the tube wall, the longer the annealing time. Wall thicknesses of from about 1 mm up to about 5 mm are conceived.

[0013] Furthermore, the atmosphere of the annealing step is very important. An atmosphere comprising nitrogen will affect the content of nitrogen in the surface of the duplex stainless steel. Hence, the role of nitrogen in the atmosphere is to maintain the nitrogen content of the material at the surface. At the annealing temperature of the present method, nitrogen will diffuse into and out from the material. The nitrogen content should be selected so that the nitrogen content in the surface is maintained. It has been found that too low nitrogen content in the atmosphere where the annealing is performed will result in a net loss of nitrogen in the surface, which will affect the corrosion resistance and the mechanical properties of the duplex stainless steel as defined hereinabove or hereinafter negatively. It has also been found that too high nitrogen levels in the atmosphere where annealing is performed will result in an increase of nitrogen in the surface of the material during annealing and as nitrogen is a strong austenite former, a change in the nitrogen content may therefore influence the phase balance. Hence, a high content of nitrogen in the atmosphere will provide for the formation of austenite in the surface. The nitrogen content in the surface of the material will also influence the structure stability with respect to the sensitivity of forming precipitates, such as chromium nitrides. The formation of precipitates will have a negative impact on the corrosion resistance of the duplex stainless steel as defined hereinabove or hereinafter.

[0014] The pitting corrosion resistance equivalent PRE is defined as $PRE = Cr(wt\%) + 3.3Mo(wt\%) + 16N(wt\%)$. A PRE of at least about 23.0 indicates that, with the above-defined composition, all three of chromium, molybdenum and nitrogen are not allowed to be at their minimum simultaneously but must be combined such that the defined PRE-value is obtained. According to another embodiment, the PRE-value is at least about 24.0. The term "about" as used hereinabove and hereinafter indicates +/- 10% of an integer.

[0015] According to one embodiment, the temperature range of the annealing step (step g) is of from 970°C to 1040°C. According to yet another embodiment, said temperature range is of from 1000°C to 1040°C.

[0016] According to one embodiment, said annealing step comprises subjecting said tube to said temperature for a time period of from 0.5-5 minutes, such as of from 0.5 to 1.5 minutes.

[0017] According to one embodiment, the inert gas is argon or helium or a mixture thereof.

[0018] According to one embodiment, the content of nitrogen gas in the gas mixture is equal to or less than 4 vol%. According to another embodiment the content of nitrogen gas in said gas mixture is equal to or less than 3 vol%. According to yet one embodiment, the content of nitrogen gas in said gas mixture is equal to or above 1.5 vol%.

[0019] According to one embodiment, said hot extrusion step (step e) comprises subjecting said tube to hot extrusion at a temperature in the range of from 1100°C-1200°C and a cross-sectional area reduction thereof in the range of from 92-98%. According to one embodiment, said hot extrusion step (step e) comprises subjecting said tube to hot extrusion at a temperature in the range of from 1100°C-1170°C and a cross-sectional area reduction thereof in the range of from 92-98%. The cross-sectional area reduction is defined as $(\text{cross-sectional area (of tube) before extrusion} - \text{cross-sectional area after extrusion}) / (\text{cross-sectional area before extrusion})$. The extrusion temperature and deformation degree is chosen with regard to the chemical composition of the duplex stainless steel such that it will not have a detrimental effect on the microstructure of the duplex stainless steel or will result in cracks or the like therein that would be detrimental to the mechanical properties of the final product.

[0020] According to one embodiment, the cold deformation step (step f) comprises subjecting the tube to cold deformation without pre-heating the tube. According to one embodiment, said cold deformation step (step f) comprises subjecting said tube to a cross sectional area reduction thereof in the range of 50-90%. Cross-sectional area reduction is defined as $(\text{cross-sectional area (of tube) before pilgering} - \text{cross-sectional area after pilgering}) / (\text{cross-sectional area before pilgering})$. The chemical composition of the duplex stainless steel is selected to enable such cold deformation thereof without unwanted crack-generation in the material or any detrimental negative effects on the microstructure of the material.

[0021] According to one embodiment of the method as defined hereinabove or hereinafter, the cold deformation is either pilgering or cold drawing.

[0022] According to one embodiment, when the cold deformation is pilgering, the relationship between the wall thickness reduction and the outer diameter reduction of the tube is expressed as the Q-value, wherein

$$Q\text{-value} = (Wallh - Wallt) * (Odh - Wallh) / Wallh ((Odh - Wallh) - (Odt - Wallt)),$$

wherein

Wallh=hollow wall=the thickness of the wall before pilgering

Wallt=tube wall=the thickness of the wall after pilgering

Odh=hollow OD=the diameter of the tube before pilgering

Odt=tube OD=the diameter of the tube after pilgering,

and wherein Q is in the range of 0.5-2.5. If the area reduction is too high, the force will be too high and the material might crack.

[0023] According to yet another embodiment, Q is in the range of from 0.9-1.1.

[0024] According to one embodiment, said duplex stainless steel has the following composition, in weight%:

C	0.01-0.025;
Si	0.35-0.6;
Mn	0.8-1.5;
Cr	21-23.5;
Ni	3.0-5.5;
Mo	0.10-1.0;
Cu	0.15-0.70;
N	0.090-0.25;
P	less than or equal to 0.035;
S	less than or equal to 0.003;

balance Fe and unavoidable impurities.

[0025] A duplex stainless steel with this chemical composition is particularly suitable to be subjected to the above-mentioned process steps with the above-mentioned process parameters. In other words, the process steps and parameters as defined hereinabove or hereinafter are selected to be particularly suitable on a duplex stainless steel with this chemical composition and to result in a tube with properties that makes it particularly suitable in an application as GDI-rail for conduction of a fuel in a fuel injection system for injecting fuel into the combustion chamber of a combustion engine.

[0026] According to another embodiment, the tube is a tube for conduction of a fuel in a fuel injection system for injecting fuel into the combustion chamber of a combustion engine. The present disclosure may, as an alternative, be defined as a process of producing a fuel conductor in a fuel injection system for injecting fuel into the combustion chamber of a combustion engine, wherein said process comprises the method defined hereinabove and/or hereinafter for producing a tube of duplex stainless steel. Such a process includes attaching the tube of duplex stainless steel to a further structural member of said combustion engine by means of brazing. The further structural member may be metal, typically austenitic or duplex steel. The method of producing the tube, including the selection of the chemical composition of the duplex stainless steel, also aims at achieving a tube with advantageous brazing properties, in particular a low susceptibility to liquid metal induced embrittlement (LMIE) caused by liquid metal penetration. The brazing includes copper brazing, possibly in a continuous furnace at temperature in the range of from 1100°C-1140°C.

[0027] According to one embodiment, the tube has an outer diameter in the range of from 15-35 mm after said pilgering step. According to one embodiment, this tube is used as a GDI-rail in a fuel injection system for conducting fuel to be injected into the combustion chamber of a combustion engine.

[0028] According to another embodiment, the tube has an outer diameter of from 7-10 mm after said pilgering step. According to one embodiment, this tube is used as a fuel line in a fuel injection system for conducting fuel to be injected into the combustion chamber of a combustion engine.

[0029] The functions and effects of essential alloying elements of the duplex stainless steel defined hereinabove and hereinafter will be presented in the following paragraphs. The listing of functions and effects of the respective alloying elements is not to be seen as complete, but there may be further functions and effects of said alloying elements. However, it provides a view of the underlying knowledge that should be considered when designing the duplex stainless steel as well as the process parameters of a method for the production of a tube of said duplex stainless steel, in particular a duplex stainless tube aimed for conduction of a fuel in a fuel injection system for injecting fuel into the combustion chamber of a combustion engine.

[0030] **Carbon, C**, has an austenite stabilizing effect and counteracts the transformation from austenitic to martensitic structure upon deformation of the duplex stainless steel. C has a positive effect on the strength of the duplex stainless steel. Therefore, the content of C should be equal to or above 0.01 wt%. However, at too high levels, carbon tends to form unwanted carbides with other alloying elements. The content of C should therefore not be above 0.06 wt%. According

to one embodiment, the content of C should not be above 0.025 wt%.

[0031] Chromium, Cr, has strong impact on the corrosion resistance of the duplex stainless steel, especially pitting corrosion. According to the present disclosure, the PRE-value is above 23.0. Moreover, Cr improves the yield strength, and counteracts transformation of austenitic structure to martensitic structure upon deformation of the duplex stainless steel. Therefore, the content of Cr should be equal to or above 21.0 wt%. At high levels, an increasing content of Cr results in a higher temperature for unwanted stable sigma phase and a more rapid generation of sigma phase. Therefore, the content of Cr is equal to or less than 24.5 wt%. Cr also has a ferrite-stabilizing effect on the duplex stainless steel. According to one embodiment the content of Cr is equal to or less than 23.5 wt%.

[0032] Nickel, Ni, has a positive effect on the resistance against general corrosion. Ni also has a strong austenite-stabilizing effect and counteracts transformation from austenitic to martensitic structure upon deformation of the duplex stainless steel. The content of Ni is therefore equal to or more than 2.0 wt%. According to another embodiment the content of Ni is equal to or more than 3.5 wt%. To some extent the austenite-stabilizing effect of Ni may be compensated for by adjusting the Cr content. The content of Ni should, however, not be more than or equal to 5.5 wt%.

[0033] Silicon, Si, is often present in the duplex stainless steel since it may have been used for deoxidization of the steel melt. Si is a ferrite stabilizer but also counteracts transformation of austenite to martensite in connection to deformation of the duplex stainless steel. It may also improve the corrosion resistance in some environments. However, Si reduces the solubility of nitrogen and carbon and may form unwanted silicides if present at too high levels. Therefore, according to one embodiment, the content of Si in the duplex stainless steel is not more than 1.5 wt%. According to one embodiment, the content of Si in the duplex stainless steel is not more than 0.6 wt%. According to one embodiment the content of Si may be as low as about 0 wt%. According to one embodiment, the content of Si should be equal to or more than 0.35 wt%.

[0034] Molybdenum, Mo, has a strong influence on the corrosion resistance of the duplex stainless steel. It heavily influences the PRE thereof. Mo is added in amount of equal to or more than 0.01 wt%. It also has a ferrite-stabilizing effect on the duplex stainless steel. According to one embodiment, the content of Mo is above 0.10 wt%. Mo also increases the temperature at which unwanted sigma-phases are stable and promotes the rate of generation thereof. It is also a relatively expensive alloying element. Therefore, the content of Mo should be equal to or less than 1.0 wt%.

[0035] Copper, Cu, has a positive effect on the corrosion resistance. Cu also counteracts transformation of austenite to martensite upon deformation of the duplex stainless steel. It is thus optional to purposively add Cu to the duplex stainless steel. Often, Cu is present in scrapped goods used for the production of steel, and is allowed to remain in the steel at moderate levels. According to one embodiment, the content of Cu may be equal to or more than 0.01 wt%. According to another embodiment, the content of Cu is equal to or more than 0.15 wt%. According to one embodiment, the content of Cu is equal to or less than 1.0 wt%. According to another embodiment, the content of Cu is equal to or less than 0.7 wt%.

[0036] Manganese, Mn, has a deformation hardening effect on the duplex stainless steel, and it counteracts the transformation from austenitic to martensitic structure upon deformation of the duplex stainless steel. Mn also has an austenite stabilizing effect. According to one embodiment, the content of Mn in the duplex stainless steel should be equal to or above 0.8 wt%. However, Mn has a negative impact on the corrosion resistance in acids and chloride-containing environments, and it increases the tendency to generation of intermetallic phases. Therefore, the maximum content of Mn should not be above 2.0 wt%. According to one embodiment, the content of Mn is equal to or less than 1.0 wt%.

[0037] Nitrogen, N, has a positive effect on the corrosion resistance of the duplex stainless steel and also contributes to deformation hardening. It has a strong effect on the pitting corrosion resistance equivalent PRE. It also has a strong austenite stabilizing effect and counteracts transformation from austenitic structure to martensitic structure upon plastic deformation of the duplex stainless steel, and is therefore added in an amount of 0.05 wt% or higher. According to one embodiment, the content of N should be equal to or more above 0.090 wt%. At too high levels, N tends to form chromium nitrides in the duplex stainless steel, which should be avoided due to its negative effect on ductility and corrosion resistance. Therefore, the content of N should be equal to or lower than 0.3 wt%. According to one embodiment, the content of N is equal to or less than 0.25 wt%.

[0038] Phosphorus, P, is an impurity contained in the duplex stainless steel and it is well known that P affects the hot workability negatively. Accordingly, the content of P is set at 0.03 wt% or less.

[0039] Sulphur, S, is an impurity contained in the austenitic stainless steel and it will deteriorate the hot workability. Accordingly, the allowable content of S is less than or equal to 0.03 wt%, such as less than or equal to 0.005 wt%.

[0040] The duplex stainless steel as defined hereinabove or herein after may optionally comprise one or more of the following elements selected from the group of Al, V, Nb, Ti, O, Zr, Hf, Ta, Mg, Ca, La, Ce, Y and B. These elements may be added during the manufacturing process in order to enhance e.g. deoxidation, corrosion resistance, hot ductility or machinability. However, as known in the art, the addition of these elements has to be limited depending on which element is present. Thus, if added the total content of these elements is less than or equal to 1.0 wt%.

[0041] The term "impurities" as referred to herein is intended to mean substances that will contaminate the duplex

EP 3 280 826 B1

stainless steel when it is industrially produced, due to the raw materials such as ores and scraps, and due to various other factors in the production process, and are allowed to contaminate within the ranges not adversely affecting the duplex stainless steel as defined hereinabove or hereinafter.

[0042] The present disclosure is further illustrated by the following non-limiting examples.

EXAMPLES

[0043] Two melts were made having the following compositions: Fe is the balance for both

No	c	Si	Mn	P	S	Cr	Ni	Mo	Cu	N
1	0.02	0.5	1.5	<0.035	<0.010	22.2	3.3	0.25	0.25	0.15
2	0.01	0.53	1.09	0.026	<0.003	22.88	3.15	0.12	0.21	0.25

[0044] The obtained melts were then processed accordingly:

They were casted to bodies by using continuous casting.

Round bars were then formed by forging and the tubes were then formed by boring a hole therein. The diameter of the tubes was then reduced by using hot extrusion at a temperature in the range of from 1120°C-1150°C, the obtained tubes had a cross-sectional area reduction of 96-98%. The hot extrusion was followed by pickling to remove glass beads. The diameter was further reduced by pilgering and subjecting the tubes to a cross sectional area reduction thereof in the range of 80-86%.

The pilgered tubes were then annealed in an atmosphere consisting of a gas mixture comprising about 2% nitrogen gas and remainder argon gas and subjecting the tubes to a temperature of about 1030°C for a time period of about 1 minute.

[0045] In the pilgering step Q is about 1.0.

[0046] After annealing, the obtained tubes were subjected to a straightening step. Straightening was performed in a roll straightening machine with a combination of bending and ovalization. The tubes were passed through a series of angled rollers which rotated the tube and applied to it a series of bending movements. During straightening the yield strength is exceeded in order to get a permanent change in shape to obtain a straight tube.

[0047] The obtained tubes had an outer diameter in the of 30 mm and the tubes are to be used as a GDI-rail in a fuel injection system for conducting fuel to be injected into the combustion chamber of a combustion engine.

[0048] One additional tube of melt 1 was also manufactured according to the method disclosed above. This tube had an outer diameter of from 8 mm after the pilgering step. This tube was also used as a fuel line in a fuel injection system for conducting fuel to be injected into the combustion chamber of a combustion engine.

Claims

1. A method of producing a tube of duplex stainless steel comprising the following composition, in weight%,

C	max 0.06;
Cr	21-24.5;
Ni	2.0-5.5;
Si	max 1.5;
Mo	0.01-1.0
Cu	0.01-1.0;
Mn	max 2.0;
N	0.05-0.3;
P	max 0.04;
S	max 0.03; and

balance Fe and unavoidable impurities,
and having a PRE-value of at least 23.0,
wherein the method comprises the steps of:

a) providing a melt of the duplex stainless steel;

EP 3 280 826 B1

- b) casting a body of the duplex stainless steel from the melt;
c) forming a bar of the body;
d) forming a tube of the bar by generating a hole therein;
e) reducing the diameter and/or wall thickness of the tube by hot extrusion at a temperature in the range of from 1100°C to 1200°C and a cross-sectional area reduction in the range of from 92-98%.;
f) further reducing the diameter and/or wall thickness of the tube by cold deformation by subjecting the tube to a cross sectional area reduction in the range of from 50-95%, and
g) annealing the cold deformed tube;

wherein after step g), the duplex stainless steel of the obtained tube consists of 40-60% austenite and 40-60% ferrite and wherein step g) comprises subjecting said tube to a temperature in the range of from 950°C-1060°C for a time period of from 0.3-10 minutes and to an atmosphere consisting of a gas mixture comprising 1-6 vol% nitrogen gas and the remainder is H₂ or an inert gas.

2. The method according to claim 1, wherein the temperature is in the range is of from 970°C-1040°C.
3. The method according to claim 1, wherein said the temperature is in the range is of from 1000°C-1040°C.
4. The method according to any one of claims 1 to 3, wherein said the annealing step comprises subjected said tube to said temperature for a time period of from 0.5 to 5 minutes.
5. The method according to any one of claims 1 to 4, wherein said the inert gas is argon or helium or a mixture thereof.
6. The method according to any one of claims 1 to 5, wherein the content of nitrogen gas in said the gas mixture is equal to or less than 4 vol%.
7. The method according to any one of claims 1 to 6, wherein the content of nitrogen gas in the gas mixture is equal to or above 1.5 vol%.
8. The method according to any one of claims 1- 7, wherein step f comprises subjecting, without pre-heating, the tube to cold deformation.
9. The method according to any one of claims 1 to 8, wherein the cold deformation is pilgering.
10. A method according to claim 9, wherein, in said pilgering step, the relationship between the wall thickness reduction and the outer diameter reduction of the tube is expressed as the Q-value, wherein

$$Q\text{-value} = (Wallh - Wallt) * (Odh - Wallh) / Wallh ((Odh - Wallh) - (Odt - Wallt)),$$

wherein

Wallh=hollow wall=the thickness of the wall before pilgering
Wallt=tube wall=the thickness of the wall after pilgering
Odh=hollow OD=the diameter of the tube before pilgering
Odt=tube OD=the diameter of the tube after pilgering,
and wherein Q is in the range of from 0.5-2.5.

11. A method according to claim 10, wherein Q is in the range of from 0.9-1.1.
12. A method according to any one of claims 1- 11, wherein said duplex stainless steel comprises, in weight%:

C	0.01-0.025;
Si	0.35-0.6;
Mn	0.8-1.5;
Cr	21-23.5;
Ni	3.0-5.5;

(continued)

5	Mo	0.10-1.0;
	Cu	0.15-0.70;
	N	0.090-0.25;
	P	less than or equal to 0.035;
	S	less than or equal to 0.003;

10 balance Fe and unavoidable impurities.

13. Use of a tube which has been manufactured according to the method according to any one of claims 1- 12 for conduction of a fuel in a fuel injection system for injecting fuel into the combustion chamber of a combustion engine.

15 **Patentansprüche**

1. Verfahren zur Herstellung eines Rohres aus rostfreiem Duplexstahl, der, nach Gew.-%, folgende Zusammensetzung umfasst

20	C	max. 0,06;
	Cr	21- 24,5;
	Ni	2, 0-5, 5;
	Si	max. 1,5;
25	Mo	0,01-1,0
	Cu	0,01-1,0;
	Mn	max. 2,0;
	N	0,05-0,3;
	P	max. 0,04;
30	S	max. 0,03; und

Rest Fe und unvermeidbare Verunreinigungen,
und mit einem PRE-Wert von mindestens 23,0,
wobei das Verfahren die folgenden Schritte umfasst:

- a) Bereitstellen einer Schmelze des rostfreien Duplexstahls;
- b) Gießen eines Körpers aus dem rostfreien Duplexstahl aus der Schmelze;
- c) Bilden eines Stabes aus dem Körper;
- 40 d) Bilden eines Rohres aus dem Stab durch Erzeugen eines Loches darin;
- e) Verringern des Durchmessers und/oder der Wanddicke des Rohres durch Warmstrangpressen mit einer Temperatur im Bereich von 1100 °C bis 1200 °C und einer Querschnittsflächenverringern im Bereich von 92 bis 98 %;
- f) weiteres Verringern des Durchmessers und/oder der Wanddicke des Rohres durch eine Kaltverformung des Rohres durch ein Unterziehen des Rohres einer Querschnittsflächenverringern im Bereich von 50 bis 95 %, und
- 45 g) Glühen des kaltverformten Rohres;

wobei der rostfreie Duplexstahl des erhaltenen Rohres nach Schritt g) aus 40-60 % Austenit und 40-60 % Ferrit besteht, und wobei Schritt g) das Aussetzen des Rohres einer Temperatur im Bereich von 950 °C bis 1060 °C für einen Zeitraum von 0,3 bis 10 Minuten und einer Atmosphäre, die aus einem Gasgemisch mit 1-6 Vol.-% Stickstoffgas und einem Rest aus H₂ oder einem Inert gas besteht, umfasst.

- 2. Verfahren nach Anspruch 1, wobei die Temperatur im Bereich von 970 °C bis 1040 °C liegt.
- 55 3. Verfahren nach Anspruch 1, wobei die Temperatur im Bereich von 1000 °C bis 1040 °C liegt.
- 4. Verfahren nach einem der Ansprüche 1 bis 3, wobei der Glühschritt ein Aussetzen des Rohres der Temperatur für

EP 3 280 826 B1

einen Zeitraum von 0,5 bis 5 Minuten umfasst.

5. Verfahren nach einem der Ansprüche 1 bis 4, wobei das Inert gas Argon oder Helium oder ein Gemisch davon ist.

5 6. Verfahren nach einem der Ansprüche 1 bis 5, wobei der Stickstoffgasgehalt in dem Gasgemisch kleiner als oder gleich 4 Vol.-% ist.

7. Verfahren nach einem der Ansprüche 1 bis 6, wobei der Stickstoffgasgehalt in dem Gasgemisch größer als oder gleich 1,5 Vol.-% ist.

10 8. Verfahren nach einem der Ansprüche 1 bis 7, wobei Schritt f) das Unterziehen des Rohres einer Kaltverformung ohne Vorwärmung umfasst.

9. Verfahren nach einem der Ansprüche 1 bis 8, wobei die Kaltverformung Pilgern ist.

15 10. Verfahren nach Anspruch 9, wobei in dem Pilgerschritt das Verhältnis zwischen der Wanddickenverringern und der Außendurchmesserverringern des Rohres als der Q-Wert ausgedrückt wird, wobei

20
$$Q\text{-Wert} = \frac{(Wandh - Wandr) * (Adh - Wandh)}{Wandh * ((Adh - Wandh) - (Adr - Wandr))},$$

wobei

25 Wandh = Hohlwand = Dicke der Wand vor dem Pilgern

Wandr = Rohrwand = Dicke der Wand nach dem Pilgern

Adh = Außendurchmesser hohl = Durchmesser des Rohres vor dem Pilgern

Adr = Außendurchmesser Rohr = Durchmesser des Rohres nach dem Pilgern,

und wobei Q im Bereich von 0,5 bis 2,5 liegt.

30

11. Verfahren nach Anspruch 10, wobei Q im Bereich von 0,9 bis 1,1 liegt.

12. Verfahren nach einem der Ansprüche 1 bis 11, wobei der rostfreie Duplexstahl, in Gew.-%, Folgendes umfasst:

35

C 0,01-0,025;

Si 0,35-0,6;

Mn 0,8-1,5;

Cr 21-23,5;

Ni 3,0-5,5;

40

Mo 0,10-1,0;

Cu 0,15-0,70;

N 0,090-0,25;

P weniger als oder gleich 0,035;

45

S weniger als oder gleich 0,003;

Rest Fe und unvermeidbare Verunreinigungen.

50 13. Verwendung eines Rohres, das gemäß dem Verfahren nach einem der Ansprüche 1 bis 12 hergestellt worden ist, zum Leiten eines Kraftstoffs in einem Kraftstoffeinspritzsystem zum Einspritzen von Kraftstoff in die Brennkammer eines Verbrennungsmotors.

55 Revendications

1. Procédé de production d'un tube d'acier inoxydable duplex comprenant la composition suivante, en % en poids,

EP 3 280 826 B1

5	C	max 0,06 ;
	Cr	21-24,5 ;
	Ni	2,0-5,5 ;
	Si	max 1,5 ;
	Mo	0,01-1,0
	Cu	0,01-1,0 ;
	Mn	max 2,0 ;
10	N	0,05-0,3 ;
	P	max 0,04 ;
	S	max 0,03 ; et

15 équilibre en Fe et impuretés inévitables,
et ayant une valeur PRÉLIMINAIRE d'au moins 23,0,
dans lequel le procédé comprend les étapes de :

- 20 a) la fourniture d'une fonte de l'acier inoxydable duplex ;
b) le moulage d'un corps de l'acier inoxydable duplex à partir de la fonte ;
c) la formation d'une barre du corps ;
d) la formation d'un tube de la barre par la génération d'un trou dans celle-ci ;
e) la réduction du diamètre et/ ou de l'épaisseur de paroi du tube par extrusion chaude à une température dans
la plage de 1 100°C et 1 200°C et une réduction de la zone transversale dans la plage de 92-98% ;
25 f) la réduction supplémentaire du diamètre et/ ou de l'épaisseur de paroi du tube par déformation à froid par la
soumission du tube à une réduction de la zone transversale dans la plage de 50 à 95 %, et
g) le recuit du tube déformé à froid ;

30 dans lequel, après l'étape g), l'acier inoxydable duplex du tube obtenu est constitué de 40-60% d'austénite et de
40-60% de ferrite et dans lequel l'étape g) comprend la soumission dudit tube à une température dans la plage de
950°C-1 060°C pendant une période de temps de 0,310 minutes et à une atmosphère constituée d'un mélange de
gaz comprenant 1-6 % en vol. de gaz d'azote et le reste est du H₂ ou un gaz inerte.

- 35 2. Procédé selon la revendication 1, dans lequel la température est dans la plage de 970 °C-1040 °C.
3. Procédé selon la revendication 1, dans lequel la température est dans la plage de 1000 °C-1 040°C.
4. Procédé selon l'une quelconque des revendications 1 à 3, dans lequel l'étape de recuit comprend ledit tube soumis
à ladite température pendant une période de temps de 0,5 à 5 minutes.
- 40 5. Procédé selon l'une quelconque des revendications 1 à 4, dans lequel le gaz inerte est de l'argon ou de l'hélium
ou un mélange de ceux-ci.
6. Procédé selon l'une quelconque des revendications 1 à 5, dans lequel la teneur en gaz d'azote dans le mélange
gazeux est égale ou inférieure à 4 % en vol.
- 45 7. Procédé selon l'une quelconque des revendications 1 à 6, dans lequel la teneur en gaz d'azote dans le mélange
gazeux est égale ou supérieure à 1,5 % en vol.
- 50 8. Procédé selon l'une quelconque des revendications 1- 7, dans lequel l'étape f comprend la soumission, sans pré-
chauffage, du tube à la déformation à froid.
9. Procédé selon l'une quelconque des revendications 1 à 8, dans lequel la déformation à froid est un laminage.
- 55 10. Procédé selon la revendication 9, dans lequel, dans ladite étape de laminage, la relation entre la réduction de
l'épaisseur de paroi et la réduction de diamètre extérieur du tube est exprimée comme valeur Q, dans laquelle

EP 3 280 826 B1

Valeur $Q = (Wallh - Wallt) * (Odh - Wallh) / Wallh ((Odh - Wallh) - (Odt - Wallt))$,

5 dans lequel

Wallh=paroi creuse=l'épaisseur de la paroi avant laminage

Wallt=paroi du tube=l'épaisseur de la paroi après laminage

Odh=OD creux=diamètre du tube avant laminage

10 Odt=OD du tube=le diamètre du tube après laminage,
et dans lequel Q est compris entre 0,5-2,5.

11. Procédé selon la revendication 10, dans lequel Q se situe dans la plage de 0,9-1,1.

15 12. Procédé selon l'une quelconque des revendications 1-11, dans lequel ledit acier inoxydable duplex comprend, en % en poids, :

20	C	0,01-0,025 ;
	Si	0,35-0,6 ;
	Mn	0,8-1,5 ;
	Cr	21-23,5 ;
	Ni	3,0-5,5 ;
25	Mo	0,10-1,0 ;
	Cu	0,15-0,70 ;
	N	0,090-0,25 ;
	P	inférieur ou égal à 0,035 ;
	S	inférieur ou égal à 0,003 ;
30		équilibre en Fe et impuretés inévitables.

35 13. Utilisation d'un tube qui a été fabriqué selon l'une quelconque des revendications 1-12 pour la conduction d'un carburant dans un système d'injection de carburant pour l'injection de carburant dans la chambre de combustion d'un moteur à combustion.

40

45

50

55

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- JP S63255322 B [0004]