

(11) **EP 2 924 131 A1**

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication: 30.09.2015 Bulletin 2015/40

(21) Application number: 14162191.2

(22) Date of filing: 28.03.2014

(51) Int CI.:

C21D 8/02 (2006.01) C2 C22C 38/02 (2006.01) C2 C22C 38/42 (2006.01) C2 C22C 38/50 (2006.01) C2

C22C 38/58 (2006.01)

C22C 38/00 (2006.01) C22C 38/06 (2006.01) C22C 38/44 (2006.01)

C22C 38/54 (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

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(54) Austenitic stainless steel

(57) The invention relates to an austenitic high-manganese stainless steel having high strength and ductility. The stainless steel which consists of in weight % 0,03 - 0,1 % carbon, 0,08 - 1,0 % silicon, 14 - 26 % manganese. 10,5 - 18 % chromium, less than 0,8 % nickel, 0,05 - 0,6

% copper, 0,1 - 0,8 % nitrogen and 0,0008 - 0,005 % boron, the rest being iron and inevitable impurities occurred in stainless steels, and the stainless steel is cold deformable utilizing the TWIP (TWinning Induced Plasticity) mechanism.

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Description

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[0001] The invention relates to an austenitic high-manganese stainless steel having high strength and high ductility which stainless steel utilizes the TWIP (TWinning Induced Plasticity) mechanism during the deformation process.

[0002] The austenitic stainless steels, such as the most versatile and widely used 304 austenitic stainless steel, have a significantly lower strength combined with relatively high residual elongation after cold deformation, such as cold rolling. The ferritic austenitic duplex stainless steels, such as the 2304 ferritic austenitic duplex stainless steel, offer a high strength, but loose ductility with even a low cold deformation degree.

[0003] The austenitic manganese stainless steels with high carbon content are vulnerable to intergranular corrosion after welding in the weld and heat-affected zone due to chromium depletion in this area. Further, the typical manganese stainless steels are in general vulnerable to form martensitic phase after cold deformation, which could lead to delayed cracking.

[0004] A twinning in the microstructure of a metal material is in general defined as two separate crystals that share some of the same crystal lattice. The TWIP (TWinning Induced Plasticity) stainless steels have austenitic microstructure with face-centered cubic lattice (FCC) along with a relatively low stacking fault energy (SFE) promoting the activation of twinning deformation mechanism, i.e. mechanically induced twinning in the crystal lattice. The term TWIP indicates that twinning often goes along with accommodation plasticity via lattice dislocations.

[0005] The object of the present invention is to eliminate some drawbacks of the prior art and to achieve an improved austenitic high-manganese stainless steel which utilizes the TWIP (TWinning Induced Plasticity) mechanism in the cold deformation in order to have a high work-hardening rate and good corrosion resistance with low vulnerability for intergranular corrosion after welding and for delayed cracking and stress corrosion cracking. The essential features of the austenitic stainless steel are enlisted in the appended claims.

[0006] According to the invention the austenitic high-manganese stainless steel consists of in weight % 0,03 - 0,1 % carbon, 0,08 - 1,0 % silicon, 14 - 26 % manganese. 10,5 - 18 % chromium, less than 0,8 % nickel, 0,05 - 0,6 % copper, 0,1 - 0,8 % nitrogen and 0,0008 - 0,005 % boron, the rest being iron and inevitable impurities occurred in stainless steels. The austenitic stainless steel of the invention further contains optionally 0,001 - 0,02 % titanium and optionally less than 0,04 % aluminium. The austenitic stainless steel of the invention has a superior ductility and high strength after plastic deformation utilizing in the cold deformation the TWIP (TWinning Induced Plasticity) mechanism. The austenitic stainless steel of the invention combines thus a high strength in the initial annealed state and a high work hardening rate with a high elongation after the cold deformation, such as cold rolling, in connection with a low nickel content.

[0007] The ranges for the yield strength $R_{p0,2}$ and the tensile strength R_m as well as the elongation to fracture A_{80} at the annealed state the austenitic high-manganese stainless steel in accordance with the invention are 470 - 600 MPa for $R_{p0,2}$, 800 - 930 MPa for R_m and 40 - 60 % for A_{80} after annealed at the temperature range of 1000 - 1150 °C. When the austenitic stainless steel in accordance with the invention was further cold deformed, such as cold rolled, the effect of TWIP (TWinning Induced Plasticity) mechanism can be shown by means of the respective ranges for the yield strength $R_{p0,2}$ and the tensile strength R_m as well as the elongation to fracture A_{80} enlisted in the following table 1 after the cold rolling with the reduction degrees of 10 % and 20 %:

Table 1

| Deformation degree | R _{p0,2} (MPa) | R _m (MPa) | A ₈₀ (%) |
|--------------------|-------------------------|----------------------|---------------------|
| 10% | 800-900 | 900-1030 | 25 - 35 |
| 20 % | 1000-1100 | 1100-1250 | 10-20 |

[0008] The austenitic high-manganese stainless steel of the invention has a high work-hardening rate of at least 20 % with the deformation degree 10 % and at least 40 % with the deformation degree 20 % for the yield strength $R_{po,2}$. Further, the elongation to fracture A_{80} is 25 - 35 % with the deformation degree 10 % and 10 - 20 % with the deformation degree 20 % showing the good ductility.

[0009] The effects of the main elements in the chemical composition of the austenitic high-manganese stainless steel according to the invention are described, the ranges being in weight %, if not otherwise mentioned.

[0010] Carbon (C) is a valuable austenite forming and stabilizing element, which enables reduced use of expensive elements nickel and copper. The upper limit for carbon alloying (less than 0,1 %) is set by the risk of carbide precipitation, which deteriorates the corrosion resistance of the stainless steel. The carbon content is low enough to maintain good corrosion resistance. The reduction of the carbon content to low levels by the decarburization process is non-economical, and therefore, the carbon content shall not be less than 0,03 %.

[0011] Silicon (Si) is added to stainless steels for deoxidizing purposes during melting and should not be below 0,08 %. Because silicon is a ferrite forming element, its content must be limited below 1 %.

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[0012] Manganese (Mn) is a key element of the austenitic stainless steel of the invention, ensuring the stable austenitic crystal structure and enabling the twinning mechanism and, further, the reduction of the use of more expensive nickel. Manganese also increases the solubility of nitrogen to the stainless steel. Plastic deformation accompanied with twinning deformation easily occurs in the case of an amount of manganese of 14 % or more without deformed structure, i.e. the strain-induced martensite. A high manganese content makes the decarburization process of the steel more difficult, impairs the surface quality and reduces the corrosion resistance of the steel. Therefore the manganese content shall be less than 26 %.

[0013] Chromium (Cr) is responsible of ensuring corrosion resistance of a stainless steel. Therefore, the chromium content in this stainless steel shall be at the minimum 10,5 %. Chromium is important in terms of avoiding the delayed cracking phenomenon. By increasing the content from this level the corrosion resistance of the steel can be improved. However, because chromium is a ferrite forming element, the increasing of the chromium content increases the need for expensive austenite formers, such as nickel and manganese or necessitates impractically high carbon and nitrogen contents. Therefore, the chromium content shall be lower than 18 %. Chromium also increases the solubility of nitrogen. [0014] Nickel (Ni) is a strong austenite former and stabilizer, but nickel is an expensive element. However, very low nickel contents would necessitate impractically high alloying with the other austenite forming and stabilizing elements. Therefore, the nickel content shall be preferably lower than 0,8 % but preferably less than 0,5 %.

[0015] Copper (Cu) is present as a residual of 0,1 - 0,6 %. Copper is a weak stabilizer of the austenite phase but, however, has a strong effect on the resistance to martensite formation. Copper also has a positive effect on ductility and forming properties.

[0016] Nitrogen (N) is a strong austenite former and stabilizer. Therefore, nitrogen alloying improves the cost efficiency of the steel by enabling lower use of nickel and copper. In order to ensure reasonably low use of the above-mentioned alloying elements, nitrogen content shall be at least 0,1 %. High nitrogen contents increase the strength of the steel and thus make forming operations more difficult. Furthermore, risk of nitride precipitation increases with increasing nitrogen content. For these reasons, the nitrogen content shall not exceed 0,8 %, preferably the nitrogen content shall be lower than 0,6 %. Nitrogen increases the stacking fault energy (SFE), which is used for the prediction of the TWIP-effect, and thus enables for and facilitates the TWIP-effect.

[0017] The austenitic stainless steel according to the invention does not form during cold rolling any deformation martensite at the room temperature or above. Therefore, the stainless steel of the invention has a high ductility. The austenitic stainless steel according to the invention is also free of stress corrosion cracking and delayed cracking, just even after aging process in air and also in 5 % sodium chloride (NaCl) environment.

Example

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[0018] The austenitic stainless steel in accordance with invention was melted in the production scale and then cast into a slab form with the chemical composition in weight %

Table 2

| С | ; | Si | Mn | Cr | Мо | Ni | Ti | Cu | Al | N | В |
|---|-----|-----|----|----|------|-----|-------|-----|------|------|--------|
| 0 | .08 | 0.5 | 20 | 13 | 0.02 | 0.2 | 0.003 | 0.5 | 0.01 | 0.43 | 0.0023 |

[0019] The slabs were further hot rolled into the thickness of 4,0 mm and then annealed at the temperature 1080 °C. The austenitic stainless steel of the invention was further cold rolled with the rolling degree of 50 % to the thickness of 2,0 mm and annealed at the temperature 1080 °C. The annealed strip product was then tested by determining the yield strength $R_{n0.2}$ and the tensile strength R_m as well as the elongation to fracture A_{80} .

[0020] In order to utilize the TWIP effect in the austenitic stainless steel of the invention the stainless steel strip was cold deformed with the reduction degree of 10 % and then determined the yield strength $R_{p0,2}$ and the tensile strength R_{m} as well as the elongation to fracture A_{80} . The respective actions were also made for the cold deformed strip having the reduction degree of 20 %. The results for those test results are described in the following table:

Table 3

| Reduction degree | R _{p0,2} (MPa) | R _m (MPa) | A ₈₀ (%) |
|------------------|-------------------------|----------------------|---------------------|
| 0% | 500 | 830 | 48 |
| 10% | 800 | 950 | 28 |
| 20 % | 1020 | 1180 | 14 |

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[0021] The results show that the austenitic stainless steel in accordance with the invention has high work-hardening rate for the yield strength $R_{p0,2}$. Further, the elongation to fracture A_{80} is 28 % with the deformation degree 10 % and 14 % with the deformation degree 20 % shows still a good ductility at high strength after cold rolling.

[0022] The austenitic stainless steel of the invention can be manufactured as slabs, blooms, billets and flat products such as coils, strips, plates, sheets, and long products such as bars, rods, wires, profiles and shapes, and tubular products such as pipes, tubes and can be applied for instance in automotive construction, tanks and crash relevant parts, construction and rail vehicles.

[0023] The high-manganese austenitic stainless steel in accordance with the invention can be cold deformed in the state of as hot strip annealed, as cold strip annealed and as hot and cold strip annealed and cold rolled in order to utilize the TWIP effect for higher yield and tensile strength values with still high ductility.

Claims

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- 1. Austenitic high-manganese stainless steel having high strength and ductility, **characterized in that** the stainless steel which consists of in weight % 0,03 0,1 % carbon, 0,08 1,0 % silicon, 14 26 % manganese. 10,5 18 % chromium, less than 0,8 % nickel, 0,05 0,6 % copper, 0,1 0,8 % nitrogen and 0,0008 0,005 % boron, the rest being iron and inevitable impurities occurred in stainless steels, is cold deformable utilizing the TWIP (TWinning Induced Plasticity) mechanism.
 - 2. Austenitic high-manganese stainless steel according to the claim 1, **characterized in that** at the annealed state the ranges for the yield strength $R_{p0,2}$ and the tensile strength R_m as well as the elongation to fracture A_{80} for the austenitic ferromanganese stainless steel are 470 600 MPa for $R_{p0,2}$, 800 930 MPa for R_m and 40 60 % for A_{80} .
- 3. Austenitic high-manganese stainless steel according to the claim 1 or 2, characterized in that the work-hardening rate based on the cold deformation for the yield strength R_{p0.2} is at least 20 % with the cold deformation degree 10 %.
 - **4.** Austenitic high-manganese stainless steel according to the claim 1, 2 or 3, **characterized in that** the work-hardening rate based on the cold deformation for the yield strength R_{p0,2} is at least 40 % with the cold deformation degree 20 %.
 - 5. Austenitic high-manganese stainless steel according to any of the preceding claims, **characterized in that** elongation to fracture A₈₀ is 25 35 % with the cold deformation degree 10 %.
- 6. Austenitic high-manganese stainless steel according to any of the preceding claims, characterized in that elongation to fracture A₈₀ is 10 20 % with the cold deformation degree 20 %.
 - 7. Austenitic high-manganese stainless steel according to any of the preceding claims, **characterized in that** the stainless steel contains optionally 0.001 0.02 % titanium and optionally less than 0.04 % aluminium.
- **8.** Austenitic high-manganese stainless steel according to any of the preceding claims, **characterized in that** the stainless steel is cold deformable for the TWIP effect in the state of as hot strip annealed.
 - **9.** Austenitic high-manganese stainless steel according to any of the preceding claims 1 7, **characterized in that** the stainless steel is cold deformable for the TWIP effect in the state of as cold strip annealed.
 - **10.** Austenitic high-manganese stainless steel according to any of the preceding claims 1 7, **characterized in that** the stainless steel is cold deformable for the TWIP effect in the state of as hot and cold strip annealed and cold rolled.
- 11. Austenitic high-manganese stainless steel according to any of the preceding claims, **characterized in that** the austenitic stainless steel is manufactured as slabs, blooms, billets, flat products such as coils, strips, plates, sheets, long products such as bars, rods, wires, profiles and shapes, tubular products such as pipes, tubes.
 - 12. Austenitic high-manganese stainless steel according to any of the preceding claims, characterized in that the austenitic stainless steel is applied for instance in automotive construction, tanks and crash relevant parts, construction and rail vehicles.



EUROPEAN SEARCH REPORT

Application Number

EP 14 16 2191

| | DOCUMENTS CONSID | ERED TO BE RELEVAN | IT | |
|---|---|---|--|---|
| Category | Citation of document with in of relevant passa | dication, where appropriate, ages | Relevar to claim | |
| X | FR 2 071 667 A5 (NI 17 September 1971 (* claim 2 * * tables 1,2 * * page 4, lines 12- * page 3, lines 10- | 1971-09-17) 20 * | 1-12 | INV. C21D8/02 C22C38/00 C22C38/02 C22C38/06 C22C38/42 C22C38/44 |
| Х | EP 1 069 202 A1 (SC OILFIELD T [AT]; BO CO KG [A) 17 Januar * claims 1,2,3,10,1 * paragraph [0025] | EHLER EDELSTAHL GMBH y 2001 (2001-01-17) 1,12 * | 1-12 | C22C38/50 C22C38/54 C22C38/58 |
| А | DE 10 2010 026808 A BERGAKAD [DE]) 12 January 2012 (20 * the whole documen | | CH 1-12 | |
| A | EP 2 465 954 A1 (CR 20 June 2012 (2012- * the whole documen | S HOLDINGS INC [US]) 06-20) t * | 1-12 | TECHNICAL FIELDS SEARCHED (IPC) |
| A | DE 728 159 C (BOEHL 21 November 1942 (1 * the whole documen | 942-11-21) | 1-12 | C21D C22C |
| | The present search report has be | peen drawn up for all claims Date of completion of the sea | urah . | Examiner |
| | The Hague | 13 August 201 | l | Pircher, Ernst |
| X : part Y : part docu A : tech O : non | ATEGORY OF CITED DOCUMENTS icularly relevant if taken alone icularly relevant if combined with another ment of the same category inclogical background -written disclosure mediate document | T : theory or p E : earlier pat after the fill er D : document L : document | rinciple underlying t ent document, but p ing date cited in the applicat cited for other reaso | the invention ublished on, or ion |

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO.

EP 14 16 2191

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This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent family

member(s)

Publication

date

13-08-2014

Publication

date

Patent document

cited in search report

10

15

20

25

30

35

40

45

50

| | 2071667 | A5 | 17-09-1971 | AT BE CH | 333818 754614 515334 | Α1 | 10-12- 18-01- 15-11- |
|-----------|--------------|--------|------------|----------------------------|---|----------------------|---|
| | | | | ES FR | 381409 2071667 | A1 A5 | 16-11- 17-09- |
| EP | 1069202 | A1 | 17-01-2001 | ZA AT | 7005986 | T | 28-04-1 15-12-1 |
| | | | | AT CA DE EP ES | 407882 2313975 50000903 1069202 2187434 | A1 D1 A1 T3 | 25-07-; 15-01-; 23-01-; 17-01-; 16-06-; |
| LL. DE | 102010026808 | A1 | 12-01-2012 | US NONE | 6454879 | B1 | 24-09-7 |
| EP | 2465954 | A1 | 20-06-2012 | EP US | 2465954 2012156085 | | 20-06-2 21-06-2 |
| | | | | | | | |
| DE | 728159 | C | 21-11-1942 | NONE | | | |
| DE | 728159 | C | 21-11-1942 | NONE | | | |
| DE | 728159 | C | 21-11-1942 | NONE | | | |
| DE | 728159 | C | 21-11-1942 | NONE | | | |
| DE | 728159 | C | 21-11-1942 | NONE | | | |
| | | | 21-11-1942 | | | | |