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(54) **HIGH-TENSILE MANGANESE STEEL CONTAINING ALUMINIUM, METHOD FOR PRODUCING A SHEET-STEEL PRODUCT FROM SAID STEEL AND SHEET-STEEL PRODUCT PRODUCED ACCORDING TO THIS METHOD**

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(57) **ABSTRACT**

A formable lightweight steel having improved mechanical properties and a high resistance to delayed hydrogen-induced cracking formation and hydrogen embrittlement includes the following elements (in wt. %): C 0.02 to ≤1.0; Mn 3 to 30; Si≤4; P max. 0.1; S max. 0.1; N max. 0.03; Sb 0.003 to 0.8, particularly advantageously to 0.5, as well as at least one or more of the following carbide-forming elements in the specified proportions (in wt. %): Al≤15; Cr>0.1 to 8; Mo 0.05 to 2; Ti 0.01 to 2; V 0.005 to 1; Nb 0.005 to 1; W 0.005 to 1; Zr 0.001 to 0.3; with the remainder being iron including the usual steel-accompanying elements, with the optional addition of the following elements, in wt. %: max. 5 Ni, max. 10 Co, max. 0.005 Ca, max. 0.01 B and 0.05 to 2 Cu.

HIGH-TENSILE MANGANESE STEEL CONTAINING ALUMINIUM, METHOD FOR PRODUCING A SHEET-STEEL PRODUCT FROM SAID STEEL AND SHEET-STEEL PRODUCT PRODUCED ACCORDING TO THIS METHOD

[0001] The invention relates to a high-strength, aluminium-containing manganese steel, to a method for producing a flat steel product from this steel, and to a flat steel product produced by this method.

[0002] European patent application EP 2 383 353 A2 discloses a high-strength, manganese-containing steel, a flat steel product formed from this steel and a method for producing this flat steel product. The steel consists of the elements (contents are in weight percent and relate to the steel melt): C: to 0.5; Mn: 4 to 12.0; Si: up to 1.0; Al: up to 3.0; Cr: 0.1 to 4.0; Cu: up to 4.0; Ni: up to 2.0; N: up to 0.05; P: up to 0.05; S: up to 0.01; with the remainder being iron and unavoidable impurities. Optionally, one or more elements from the group "V, Nb, Ti" are provided, wherein the sum of the contents of these elements is at most equal to 0.5. This steel is said to be characterised in that it can be produced in a more cost-effective manner than steels containing a high content of manganese and at the same time has high elongation at fracture values and, associated therewith, a considerably improved deformability. A method for producing a flat steel product from the high-strength, manganese-containing steel described above comprises the following working steps: —smelting the above-described steel melt,—producing a starting product for subsequent hot rolling, in that the steel melt is cast into a string from which at least one slab or thin slab is separated off as a starting product for the hot rolling, or into a cast strip which is supplied to the hot rolling process as a starting product,—heat-treating the starting product in order to bring the starting product to a hot rolling starting temperature of 1150 to 1000° C.,—hot rolling the starting product to form a hot strip having a thickness of at most 2.5 mm, wherein the hot rolling is terminated at a hot rolling end temperature of 1050 to 800° C.,—reeling the hot strip to form a coil at a reeling temperature of ≤700° C.

[0003] Proceeding therefrom, the object of the present invention is to provide a high-strength, aluminium-containing manganese steel having good deformation properties and an increased resistance to delayed crack formation and hydrogen embrittlement, a method for producing a flat steel product from this steel and a flat steel product produced by this method, which offer a good combination of strength and deformation properties in relation to the steel.

[0004] This object is achieved by a high-strength, aluminium-containing manganese steel having the features of claim **1**, a method for producing a flat steel product, in particular using the aforementioned steel, having the features of claim **12**, and a flat steel product produced by this method as claimed in claim **14**. Advantageous embodiments of the invention are described in the dependent claims.

[0005] In accordance with the invention, a high-strength, aluminium-containing manganese steel having the following chemical composition (in wt. %): C: 0.01 to <0.3; Mn: 4 to <10; Al: >1 to 4; Si: 0.01 to 1; Cr: 0.1 to 4; Mo; 0.02 to 1; P: <0.1; S: <0.1; N: <0.3; with the remainder being iron with unavoidable steel-associated elements, with optional alloying of one or more of the following elements (in wt. %): V: 0.01 to 1; Nb: 0.01 to 1; Ti: 0.01 to 1; Sn: 0 to 0.5; Cu: 0.005 to 3; W: 0.03 to 3; Co: 0.05 to 3; Zr: 0.03 to 0.5 and Ca: 0.0005 to 0.1 offers a good combination of strength, strain and deformation properties. Moreover, the production of this manganese steel in accordance with the invention having a medium manganese content (medium manganese steel) on the basis of the alloy elements C, Mn, Cr, Al, Si and Mo is relatively cost-effective. Owing to the increased Al content, the steel has a lower specific density compared with other manganese steels alloyed with a small amount of Al and having medium manganese contents. The manganese steel in accordance with the invention is also characterised by an increased resistance to delayed crack formation (delayed fracture) and to hydrogen embrittlement. This is achieved by a precipitation of molybdenum carbide which acts as a hydrogen trap.

[0006] The steel in accordance with the invention has a multi-phase microstructure, consisting of ferrite and/or martensite and/or bainite and residual austenite and a TRIP and/or TWIP effect. The residual austenite content is 5% to 65%. The residual austenite is partially or completely converted into martensite by the TRIP effect upon applying high mechanical stresses. Owing to the TRIP effect, the elongation at fracture, in particular uniform elongation, and tensile strength increase considerably.

[0007] The use of the term "to" in the definition of the content ranges, such as e.g. 0.01 to 1 wt. %, means that the limit values—0.01 and 1 in the example—are also included.

[0008] The steel in accordance with the invention is suitable in particular for producing higher-strength thick plates, hot and cold strips which can be provided with a metallic or non-metallic coating. Applications are feasible inter alia in the automotive industry, shipbuilding, plant design, infrastructure, the aerospace industry and in household appliances.

[0009] Advantageously, the steel has a tensile strength Rm of >800 to 1700 MPa and an elongation at fracture A50 of 6 to 45%, preferably >8 to 45%. A test piece body A50 was used for the elongation at fracture tests as per DIN 50 125.

[0010] Alloy elements are generally added to the steel in order to influence specific properties in a targeted manner. An alloy element can thereby influence different properties in different steels. The effect and interaction generally depend greatly upon the quantity, presence of further alloy elements and the solution state in the material. The correlations are varied and complex. The effect of the alloy elements in the alloy in accordance with the invention will be discussed in greater detail hereinafter. The positive effects of the alloy elements used in accordance with the invention will be described hereinafter:

[0011] Carbon C: is required to form carbides, stabilises the austenite and increases the strength. Higher contents of C impair the welding properties and result in the impairment of the strain and toughness properties, for which reason a maximum content of less than 0.3 wt. % is set. In order to achieve a sufficient strength for the material, a minimum addition of 0.01 wt. % is required.

[0012] Manganese Mn: stabilises the austenite, increases the strength and the toughness and permits a deformation-induced martensite formation and/or twinning in the alloy in accordance with the invention. Contents of less than 4 wt. % are not sufficient to stabilise the austenite and thus impair the strain properties whereas with contents of 10 wt. % and more the austenite is stabilised too much and as a result the strength properties, in particular the yield strength, are reduced. For the manganese steel in accordance with the invention having medium manganese contents, a range of 4 to <10 wt. % is preferred.

[0013] Aluminium Al: an Al content of greater than 1 wt. % improves the strength and strain properties, decreases the specific density and influences the conversion behaviour of the alloy in accordance with the invention. Contents of Al of more than 4 wt. % impair the strain properties. Higher Al contents also considerably impair the casting behaviour in the continuous casting process. This produces increased outlay when casting. At less than 4 wt. %, Al delays the precipitation of carbides. Therefore, a maximum content of 4 wt. % and a minimum content of >1 wt. % are set.

[0014] Silicon Si: impedes the diffusion of carbon, reduces the specific density and increases the strength and strain properties and toughness properties. Furthermore, an improvement in the cold-rollability could be seen by alloying Si. Contents of more than 1 wt. % result in embrittlement of the material and negatively influence the hot- and cold-rollability and the coatability e.g. by galvanising. Therefore, a maximum content of 1 wt. % and a minimum content of 0.01 wt. % are set. Preferably, a maximum content of less than 1 wt. % is set.

[0015] Chromium Cr: improves the strength and reduces the rate of corrosion, delays the formation of ferrite and perlite and forms carbides. The maximum content is set to less than 4 wt. % since higher contents result in an impairment of the strain properties. A minimum Cr content is set to 0.1 wt. %.

[0016] Molybdenum Mo: acts as a carbide forming agent, increases the strength and increases the resistance to delayed crack formation and hydrogen embrittlement. Contents of Mo of more than 1 wt. % impair the strain properties, for which reason a maximum content of 1 wt. % and a minimum content of 0.02 wt. % are set.

[0017] Phosphorus P: is a trace element from the iron ore and is dissolved in the iron lattice as a substitution atom. Phosphorous increases the hardness and improves the hardenability by means of mixed crystal solidification. However, attempts are generally made to lower the phosphorous content as much as possible because inter alia it exhibits a strong tendency towards segregation owing to its low diffusion rate and greatly reduces the level of toughness. The attachment of phosphorous to the grain boundaries can cause cracks along the grain boundaries during hot rolling. Moreover, phosphorous increases the transition temperature from tough to brittle behaviour by up to 300° C. For the aforementioned reasons, the phosphorus content is limited to less than 0.1 wt. %.

[0018] Sulphur S: like phosphorous, is bound as a trace element in the iron ore. It is generally not desirable in steel because it exhibits a strong tendency towards segregation and has a greatly embrittling effect, whereby the strain and toughness properties are impaired. An attempt is therefore made to achieve amounts of sulphur in the melt which are as low as possible (e.g. by deep vacuum treatment). For the aforementioned reasons, the sulphur content is limited to less than 0.1 wt. %.

[0019] Nitrogen N: N is likewise an associated element from steel production. In the dissolved state, it improves the strength and toughness properties in steels containing a high content of manganese of greater than or equal to 4 wt. % Mn. Lower Mn-alloyed steels of <4 wt. % with free nitrogen tend to have a strong ageing effect. The nitrogen even diffuses at low temperatures to dislocations and blocks the same. It thus produces an increase in strength associated with a rapid loss of toughness. Binding of the nitrogen in the form of nitrides is possible e.g. by alloying aluminium, vanadium, niobium or titanium. For the aforementioned reasons, the nitrogen content is limited to less than 0.3 wt. %.

[0020] Microalloy elements are generally added only in very small amounts (<0.1 wt. % per element). In contrast to the alloy elements, they mainly act by precipitation formation but can also influence the properties in the dissolved state. Despite the small amounts added, microalloy elements greatly influence the production conditions and the processing properties and final properties.

[0021] Typical microalloy elements are vanadium, niobium and titanium. These elements can be dissolved in the iron lattice and form carbides, nitrides and carbonitrides with carbon and nitrogen.

[0022] Vanadium V and niobium Nb: these act in a grain-refining manner in particular by forming carbides, whereby at the same time the strength, toughness and strain properties are improved. Contents of more than 1 wt. % do not provide any further advantages. For vanadium and niobium, a minimum content of greater than or equal to 0.02 wt. % and a maximum content of less than or equal to 1 wt. % are optionally preferred.

[0023] Titanium Ti: acts in a grain-refining manner as a carbide forming agent, whereby at the same time the strength, toughness and strain properties are improved and the inter-crystalline corrosion is reduced. Contents of Ti of more than 1 wt. % impair the strain properties, for which reason a maximum content of 1 wt. % is optionally set. Minimum contents of 0.02 wt. % may be preferred.

[0024] Tin Sn: tin increases the strength but, similar to copper, accumulates beneath the scale layer and at the grain boundaries at higher temperatures. This results, owing to the penetration into the grain boundaries, in the formation of low-melting phases and, associated therewith, to cracks in the microstructure and to solder brittleness, for which reason a maximum content of less than or equal to 0.5 wt. % and a minimum content of 0.005 wt. % are optionally provided.

[0025] Copper Cu: reduces the rate of corrosion and increases the strength. Contents of above 3 wt. % impair the producibility by forming low-melting phases during casting and hot rolling, for which reason a maximum content of 3 wt. % and a minimum content of 0.005 wt. % are optionally set. A minimum content of 0.5 wt. % is preferred.

[0026] Tungsten W: acts as a carbide forming agent and increases the strength and heat resistance. Contents of W of more than 3 wt. % impair the strain properties, for which reason a maximum content of 3 wt. % and a minimum content of 0.03 wt. % are optionally set. A minimum content of 0.05 wt. % is preferred.

[0027] Cobalt Co: increases the strength of the steel, stabilises the austenite and improves the heat resistance. Contents of more than 3 wt. % impair the strain properties, for which reason a maximum content of less than or equal to 3 wt. % and a minimum content of 0.05 wt. % are optionally set. A minimum content of 0.08 wt. % is preferred.

[0028] Zirconium Zr: acts as a carbide forming agent and improves the strength. Contents of Zr of more than 0.5 wt. % impair the strain properties, for which reason a maximum content of 0.5 wt. % and a minimum content of 0.03 wt. % are optionally set. A minimum content of 0.05 wt. % is preferred.

[0029] Calcium Ca: Calcium is used for modifying non-metallic oxidic inclusions which could otherwise result in the undesired failure of the alloy as a result of inclusions in the microstructure which act as stress concentration points and weaken the metal composite. Furthermore, Ca improves the homogeneity of the alloy in accordance with the invention. In order to achieve a corresponding effect, a minimum content of 0.0005 wt. % is optionally necessary. Contents of above 0.1 wt. % Ca do not provide any further advantage in the modification of inclusions, impair producibility and should be avoided by reason of the high vapour pressure of Ca in steel melts. Therefore, a maximum content of 0.1 wt. % is provided.

[0030] In accordance with the invention, a method for producing a flat steel product, in particular from the steel described above, comprising the steps of:

- **[0031]** smelting a steel melt containing (in wt. %): C: 0.01 to <0.3; Mn: 4 to <10; Al: >1 to 4; Si: 0.01 to 1; Cr: 0.1 to 4; Mo: 0.02 to 1; P: <0.1; S: <0.1; N: <0.3; with the remainder being iron including unavoidable steel-associated elements, with optional alloying of one or more of the following elements (in wt. %): V: 0.01 to 1; Nb: 0.01 to 1; Ti: 0.01 to 1; Sn: 0 to 0.5; Cu: 0.005 to 3; W: 0.03 to 3; Co: 0.05 to 3; Zr: 0.03 to 0.5 and Ca: 0.0005 to 0.1;
- **[0032]** casting the steel melt to form a pre-strip by means of a horizontal or vertical strip casting process approximating the final dimensions or casting the steel melt to form a slab or thin slab by means of a horizontal or vertical slab or thin slab casting process,
- **[0033]** re-heating the slab or thin slab to 1050° C. to 1250° C. and then hot rolling the slab or thin slab to form a hot strip or thick plate, or re-heating the produced pre-strip which approximates the final dimensions, in particular with a thickness of greater than 3 mm, to 1000° C. to 1200° C. and then hot rolling the pre-strip to form a hot strip or thick plate, or hot rolling the pre-strip without re-heating from the casting heat to form a hot strip or thick plate with optional intermediate heating between individual rolling passes of the hot rolling,
- **[0034]** reeling the hot strip and optionally the thick plate at a reeling temperature between 780° C. and room temperature,
- **[0035]** optionally annealing the hot strip or thick plate with the following parameters: annealing temperature: 610 to 780° C., annealing duration: 1 minute to 48 hours,
- **[0036]** optionally cold rolling the hot strip or produced pre-strip which approximates the final dimensions, with a thickness of less than or equal to 3 mm to form a cold strip,
- **[0037]** optionally annealing the cold strip with the following parameters: annealing temperature: 610 to 780° C., annealing duration: 1 minute to 48 hours, provides a flat steel product having a good combination of strength, strain and deformation properties, and an increased resistance to delayed crack formation and hydrogen embrittlement and has a TRIP and/or TWIP effect during mechanical loading owing to its residual austenite content in the microstructure.

[0038] In relation to other advantages, reference is made to the above statements relating to the steel in accordance with the invention. The method results in a steel product in the form of a thick plate, hot strip or cold strip. Provision is made that the hot strip is wound at a temperature of at most 780° C. Room temperature is provided as the lower limit because the winding temperature has only a small influence on subsequent processing properties. In the context of the present invention, strips having thicknesses of over 3 mm are defined as the thick plate, wherein these strips can certainly still be wound e.g. at a thickness of 5 mm. A thick plate having a greater thickness, e.g. 50 mm, is made into a sheet after hot rolling to form sheet material because it can no longer be wound. The hot strip or cold strip can also be made into a sheet as required.

[0039] Typically, the hot rolling end temperature is between 950° C. and A_c1+50 K.

[0040] Typically, thickness ranges for the pre-strip are 1 mm to 35 mm and for slabs and thin slabs they are 35 mm to 450 mm. Provision is preferably made that the slab or thin slab is hot rolled to form a hot strip or thick plate having a thickness of 70 mm to 1.5 mm or the cast pre-strip approximating the final dimensions is hot rolled to form a hot strip having a thickness of 8 mm to 1 mm. The cold strip in accordance with the invention has a thickness of e.g. greater than 0.15 mm.

[0041] In the context of the above method in accordance with the invention, a pre-strip produced with the two-roller casting process and approximating the final dimensions and having a thickness of less than or equal to 3 mm, preferably 1 mm to 3 mm is already understood to be a hot strip. The pre-strip thus produced as a hot strip does not have a 100% cast structure owing to the introduced deformation of the two rollers running in opposite directions. Hot rolling thus already takes place in-line during the two-roller casting process which means that separate hot rolling is not necessary.

[0042] Re-heating temperatures in the range of 720° C. to 1200° C. are provided for hot rolling of the pre-strip from the casting heat to form a hot strip with optional intermediate heating between individual rolling passes of the hot rolling process. If only a few rolling passes are necessary, the re-heating temperature can be selected at the lower end of the range.

[0043] The hot strip, like the thick plate, can optionally be subjected to a heat treatment in the temperature range between 610 and 780° C. for 1 minute to 48 hours, wherein higher temperatures are associated with shorter treatment times and vice versa. Annealing can take place both in a batch-type annealing process (longer annealing times) and e.g. in a continuous annealing process (shorter annealing times). The heat treatment can likewise be omitted if the hot strip or thick plate already has the finished usage properties.

[0044] After the annealing process, the annealed hot strip can optionally be cold-rolled with the aim of setting the thicknesses of greater than or equal to 0.15 mm as required for the end use. Subsequent thereto, a further annealing process can be performed, if necessary coupled with a coating process and finally a temper-rolling process, by means of which the surface structure required for the end use is set.

[0045] Preferably, the flat steel product is galvanised by hot-dipping or electrolytically or is coated metallically, inorganically or organically.

[0046] A flat steel product produced by the method in accordance with the invention in the form of a thick plate, hot strip or cold strip has a tensile strength Rm>800 to 1700 MPa and an elongation at fracture A50 of 6 to 45%, preferably >8 to 45%. In this case, high strengths tend to be associated with, lower elongations at fracture and vice versa.

What is claimed is:

1.-**15**. (canceled)

16. A high-strength, aluminium-containing manganese steel comprising a following chemical composition in wt. %:

C: 0.01 to <0.3
Mn: 4 to <10
Al: >1 to 4
Si: 0.01 to 1
Cr: 0.1 to 4
Mo: 0.02 to 1
P: <0.1
S: <0.1
N: <0.3

with the remainder being iron with unavoidable steel-associated elements.

17. The steel of claim **16**, further comprising at least one alloying element, in wt. %, selected from the group consisting of:

V: 0.01 to 1
Nb: 0.01 to 1
Ti: 0.01 to 1
Sn: 0 to 0.5
Cu: 0.005 to 3
W: 0.03 to 3
Co: 0.05 to 3
Zr: 0.03 to 0.5
Ca: 0.0005 to 0.1.

18. The steel of claim **16**, wherein a content of Si is 0.01 to <1.

19. The steel of claim **16**, wherein a content of V is 0.02 to 1.

20. The steel of claim **16**, wherein a content of Nb is 0.02 to 1.

21. The steel of claim **16**, wherein a content of Ti is 0.02 to 1.

22. The steel of claim **16**, wherein a content of Sn is 0.005 to 0.5.

23. The steel of claim **16**, wherein a content of Cu is 0.5 to 3.

24. The steel of claim **16**, wherein a content of W is 0.05 to 3.

25. The steel of claim **16**, wherein a content of Co is 0.08 to 3.

26. The steel of claim **16**, wherein a content of Zr is 0.05 to 0.5.

27. The steel of claim **16**, wherein the steel has a tensile strength Rm>800 to 1700 MPa and an elongation at fracture A50 of 6 to 45%.

28. The steel of claim **16**, wherein the steel has an elongation at fracture A50 of >8 to 45%.

29. A method for producing a flat steel product, comprising:

smelting a steel melt having a chemical composition comprising in wt. %:

C: 0.01 to <0.3
Mn: 4 to <10
Al: >1 to 4
Si: 0.01 to 1
Cr: 0.1 to 4
Mo: 0.02 to 1
P: <0.1
S: <0.1
N: <0.3

with the remainder being iron with unavoidable steel-associated elements;

casting the steel melt to form a pre-strip by a horizontal or vertical strip casting process approximating a final dimension or casting the steel melt to form a slab or thin slab by a horizontal or vertical slab or thin slab casting process;

re-heating the slab or thin slab to 1050° C. to 1250° C. and then hot rolling the slab or thin slab to form a hot strip or thick plate, or re-heating the pre-strip which approximates the final dimension to 1000° C. to 1200° C. and then hot rolling the pre-strip to form a hot strip or thick plate, or hot rolling the pre-strip without re-heating from the casting heat to form a hot strip or thick plate with optional intermediate heating between individual rolling passes of the hot rolling;

reeling the hot strip and optionally the thick plate at a reeling temperature between 780° C. and room temperature;

optionally annealing the hot strip or thick plate at an annealing temperature of 610 to 780° C. and annealing duration of 1 minute to 48 hours;

optionally cold rolling the hot strip or produced pre-strip which approximates the final dimensions, with a thickness of less than or equal to 3 mm to form a cold strip;

optionally annealing the cold strip at an annealing temperature of 610 to 780° C. and annealing duration of 1 minute to 48 hours.

30. The method of claim **29**, wherein the steel melt contains at least one alloying element in wt. % selected from the group consisting of:

V:0.01 to 1
Nb: 0.01 to 1
Ti: 0.01 to 1
Sn: 0 to 0.5
Cu: 0.005 to 3
W: 0.03 to 3
Co: 0.05 to 3
Zr: 0.03 to 0.5
Ca: 0.0005 to 0.1.

31. The method of claim **29**, wherein the produced pre-strip has a thickness of greater than 3 mm.

32. The method of claim **29**, wherein the slab is hot-rolled to form a hot strip having a thickness of 70 mm to 1.5 mm or the pre-strip is hot rolled to form a hot strip having a thickness of 8 mm to 1 mm.

33. A flat steel product produced by a method as set forth in claim **29**, said steel product comprising a tensile strength Rm of >800 to 1700 MPa, and an elongation at fracture A50 of 6 to 45%.

34. The steel product of claim **33**, wherein the steel product has an elongation at fracture A50 of >8 to 45%.

35. The steel product of claim **33**, wherein the steel product is galvanised by hot-dipping or electrolytically or is coated metallically, inorganically or organically.

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