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

(11) EP 3 269 831 A1

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
17.01.2018 Bulletin 2018/03

(21) Application number: **16179114.0**

(22) Date of filing: **12.07.2016**

(51) Int Cl.:
C21D 8/02 *(2006.01)* ***C21D 8/10*** *(2006.01)*
C21D 9/08 *(2006.01)* ***C21D 9/46*** *(2006.01)*
C22C 38/00 *(2006.01)* ***C22C 38/02*** *(2006.01)*
C22C 38/04 *(2006.01)* ***C22C 38/10*** *(2006.01)*
C22C 38/12 *(2006.01)* ***C22C 38/14*** *(2006.01)*
C22C 38/18 *(2006.01)* ***C22C 38/44*** *(2006.01)*
C22C 38/46 *(2006.01)* ***C22C 38/48*** *(2006.01)*
C22C 38/50 *(2006.01)* ***C22C 38/52*** *(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
Designated Validation States:
MA MD

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(54) **HIGH CHROMIUM MARTENSITIC HEAT-RESISTANT STEEL WITH COMBINED HIGH CREEP RUPTURE STRENGTH AND OXIDATION RESISTANCE**

(57) Martensitic heat-resistant steel for boiler applications with a unique combination of enhanced creep strength and excellent oxidation resistance upon high temperature exposure in steam containing environments., having the following melt analysis (in wt.-%):
C: 0.10 to 0.16%, Si: 0.20 to 0.60%, Mn: 0.30 to 0.80%, P ≤0.020%, S ≤0.010%, Al ≤0.020%, Cr: 10.5 to 12.00%, Mo: 0.10 to 0.60%, V: 0.15 to 0.30%, Ni: 0.10 to 0.40%, B: 0.008 to 0.015%, N:0.002 to 0.020%, Co: 1.50 to 3.00%, W: 1.50 to 2.50%, Nb: 0.02 to 0.07%, Ti: 0.001-0.020%. The balance of the steel consists of iron and unavoidable impurities. The steel is normalized for a period of about 10 to about 120 minutes in the temperature range between 1050 °C and 1170°C and cooled down in air or water to room temperature, and then tempered for at least one hour in the temperature range between 750°C and 820°C. It exhibits martensitic microstructure with average δ-ferrite content of less than 5 vol.-%.

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Description

[0001] The invention relates to martensitic high chromium heat-resistant steels for components operating at elevated temperatures i.e. between 550 and 750°C and high stresses. The steel according to the invention can be used in power generation, chemical and petrochemical industry.

STATE OF THE ART

[0002] The ferritic/martensitic high Cr steel materials are widely used in the modern power plants as reheater/superheater tubes and as steam pipes. Further improvement of the net efficiency of thermal power plants will require an increase of the steam parameters pressure and temperature. Therefore, the realization of more efficient power plant cycles will require stronger materials with improved steam-side oxidation resistance. The known efforts to develop new martensitic high chromium steel that combines excellent creep properties and superior oxidations resistance have failed so far due to the formation of the so called Z-phase. Z-phase is a complex nitride that coarsens quickly thereby consuming the surrounding strengthening MX precipitates, M being: Nb, V and X being: C, N.

[0003] Elevated Cr contents i.e. containing more than 9wt.-% of Cr, which are essential for good steam oxidation resistance, however, increase the driving force for Z-phase formation and also enhance the coarsening rate of chromium carbide precipitates. Both, the loss of the microstructure stabilizing effect of MX and chromium carbide precipitates are responsible for the drop in the long-term creep rupture strength of martensitic high Cr heat-resistant steel grades. Hence, the major challenge for future steel developments is to resolve the apparent contradiction between the creep rupture strength and oxidation resistance.

[0004] Currently, for high-temperature applications, ASTM Grades 91 and 92 are widely used, both containing 9 wt.-%Cr with creep rupture strengths after 10^5h at 600°C at 90 and 114MPa respectively. The main difference between the two steels is that Grade 92 contains W in the range of 1.8 wt.-% and reduced Mo of 0.4 wt.-% compared to 1 wt.-% in case of Grade 91. Additionally, Grade 92 contains small amounts of B below 0.005 wt.-%.

[0005] Both steels suffer from insufficient oxidation resistance in steam atmospheres at temperatures above 600°C, which is limiting the application temperature range significantly. Especially in boiler components with heat transfer, the oxide scale acts as thermal insulator thereby increasing the metal temperature and consequently reducing lifetime of corresponding components. Additionally, the oxide scales, if spalled off during operation, will cause erosion damage on the following steam carrying components or after entering the steam turbine on turbine blades and guiding vanes. Spalled oxide scales may cause tube blockage especially in the region of bends, impeding the steam flow often resulting in local overheating and catastrophic failure.

[0006] X20CrMoV11-1 is a well established high Cr ferritic/martensitic steel for high temperature applications containing 0.20wt.-% C, 10.5-12 wt.-percent Cr, 1 wt.-% Mo and 0.2wt.-% V. This steel exhibits oxidation properties which are better than that of ASTM steel grades 91 and 92 due to higher Cr contents, but poor creep rupture strength (creep rupture strength after 10^5h at 600°C being around 59MPa). Additionally the hot-workability and weldability are deteriorated due to high C content of 0.20 wt.-%. ASTM Grade 122 contains 10-12%Cr, 1.8%W, 1%Cu and also V, Nb and N additions to induce the precipitation of MX strengthening particles. The creep rupture strength is significantly below that of ASTM Grade 92 that presents a creep rupture strength of 98MPa after 10^5h at 600°C.

[0007] Also hot-workability issues due to elevated Cu contents are present.

[0008] Another steel with 11 to 12 wt.-% of Cr exists. it is mainly used as thin-walled tube, and is called VM12-SHCsteels that combines good steam-side oxidation resistance and the creep rupture strength at the level of ASTM Grade 91.Such steel concept is known from patent application WO02081766 disclosing a steel for high temperature use containing by weight: 0.06 to 0.20% of C, 0.10 to 1.00% of Si, 0.10 to 1.00% of Mn, not more than 0.010% of S, 10.00 to 13.00% of Cr, not more than 1.00% of Ni, 1.00 to 1.80% of W, Mo such that (W/2+Mo) is not more than 1.50%, 0.50 to 2.00% of Co, 0.15 to 0.35% of V, 0.040 to 0.150% of Nb, 0.030 to 0.12% of N, 0.0010 to 0.0100% of B and optionally up to 0.0100% of Ca, the rest of the chemical composition consisting of iron and impurities or residues resulting from or required for preparation processes or steel casting. The chemical constituent contents preferably verify a relationship such that the steel after normalizing heat treatment between 1050 and 1080 °C and tempering has a tempered martensite structure free or practically free of delta ferrite. Compared to this steel, creep rupture strength can still be improved while keeping the other properties such as corrosion resistance and mechanical properties unaffected.

OBJECT AND SOLUTION

[0009] The object of the present invention is therefore to provide a martensitic heat-resistant steel with substantially better creep rupture strength than ASTM Grade 92 steel for pipes and tubes, and with hot corrosion and steam oxidation behavior comparable or better than X20CrMoV11-1 and VM12-SHC steels, described in the state of the art.

[0010] A further object of the invention is to obtain a steel exhibiting martensitic microstructure with a limitation of the

delta ferrite, also known as δ-ferrite, content to 5 vol.-% in average.

[0011] Another object of the invention was to provide a steel that allows the fabrication of small or large diameter seamless and welded tubes and pipes, forgings and plates using the known and established manufacturing processes.

[0012] The steel is suited as a production material for whole variety of components operating under stress at elevated temperatures, particularly as seamless and welded tubes/pipes, forgings and plates in power generation, chemical and petrochemical industry. In addition, the steel according to the invention is temper resistant, after long tempering times up to 30 hours at 800°C, the yield strength is above or equal 440 MPa, the tensile stress above or equal 620 MPa and toughness at 20°C is above or equal 40 J when tested in longitudinal direction and 27 J when tested in transverse direction.

[0013] In accordance with the present invention, the object can be achieved by a steel for high-temperature applications having the following chemical composition in weight percent:

C: 0.10 to 0.16%

Si: 0.20 to 0.60%

Mn: 0.30 to 0.80%

P ≤0.020%

S ≤0.010%

Al ≤0.020%

Cr: 10.50to 12.00%

Mo: 0.10 to 0.60%

V: 0.15 to 0.30%

Ni: 0.10 to 0.40%

B: 0.008 to 0.015%

N: 0.002 to 0.020%

Co: 1.50 to 3.00%

W: 1.50 to 2.50%

Nb: 0.02 to 0.07%.

Ti: 0.001 to 0.020%, the balance of said steel being iron and unavoidable impurities.

[0014] Preferably, the ratio of boron and nitrogen is such that: $^{B}/_{N} \leq 1.5$to achieve hot workability.

[0015] Preferably, the following equation is satisfied:

$$1.00\ \% \leq \mathrm{Mo}+0.5\mathrm{W} \leq 1.50\ \%\ (\text{in wt \%}),$$

[0016] In another preferred embodiment, the following equation is satisfied (in wt.-%):

$$B - (^{11}/_{14})(N - 10^{-(1/2.45)\cdot(logB+6.81)} - (^{14}/_{48}) \cdot Ti) \geq 0.007$$

[0017] In another preferred embodiment, the following equation is satisfied (in wt.-%):

$$2.6 \leq 4 \cdot (Ni + Co + 0.5 \cdot Mn) - 20 \cdot (C + N) \leq 11.2$$

[0018] In a preferred embodiment, the carbon content is between 0.13 and 0.16%.

[0019] In another preferred embodiment, the Mo content is between 0.30 and 0.60%.

[0020] Preferably, B content is between 0.0095 and 0.013%.

[0021] In a preferred embodiment, the Ti content is between 0.001 and 0.005%.

[0022] In another preferred embodiment, the microstructure comprises in average at least 95 % of tempered martensite, the balance being delta ferrite.

[0023] In an even more preferred embodiment, the microstructure comprises in average at least 98 % of tempered martensite, the balance being delta ferrite.

[0024] In the most preferred embodiment, the microstructure is martensitic and free of delta ferrite.

[0025] The invention also relates to a method of production comprising the following steps:

- casting a steel with a chemical composition according to the invention,
- hot forming said steel,
- heating said steel and holding said steel for a time between 10 and 120 minutes in the temperature range between 1050 °C and 1170°C,
- cooling said steel down to room temperature,
- reheating said steel and holding said steel up to a tempering temperature TT that is between 750°C and 820°C for at least one hour,
- cooling said steel down to room temperature.

[0026] Preferably, the cooling step is done using air cooling or water cooling.

[0027] The invention also concerns the production of a seamless or welded tube, pipe or plate using the steel according to the invention or the process according to the invention.

[0028] Figure 1 shows the schematic of mass gain due to oxidation plotted versus chromium content.

SUBJECT MATTER OF THE INVENTION

[0029] In accordance with the present invention, a martensitic high chromium heat-resistant steel is created having the following chemical composition:

(1) C: 0.10 to 0.16%,

[0030] C needs to be added to at least 0.10 % to obtain sufficient carbide precipitation. Additionally C is also an austenite stabilizing element. C contents below 0.10% would imply more δ-ferrite in the microstructure. The upper limit for carbon is 0.16% because excess C addition limits the toughness and weldability properties.

(2) Si: 0.20 to 0.60%,

[0031] Si is used for deoxidation during the steel making process. Additionally, it is one of key elements, which determines the oxidation behavior in steels. In order to achieve the full oxidation improving effect of Si additions an amount of at least 0.20 % is necessary. The upper Si level shall preferably be limited to 0.60 %, because the excess Si addition accelerates the coarsening of precipitates and decreases toughness.

(3) Mn: 0.30 to 0.80%,

[0032] Mn is an effective deoxidation element. It ties up sulphur and reduces the δ-ferrite formation. At least 0.30% Mn may be added. The upper limit shall be 0.8%, since excessive additions reduce the strength of steels at elevated temperatures.

(4) P ≤ 0.020%,

[0033] P is a grain-boundary active element, which reduces the toughness properties of steels. The content has to be limited to 0.020% in order to avoid the negative impact of P on toughness properties.

(5) S ≤ 0.010%,

[0034] S forms sulfides and reduces the toughness and hot-workability properties of steels. A limitation of upper S content to 0.010 prevents the defect formation during hot-working operation and the negative impact on toughness.

(6) Al ≤ 0.020%,

[0035] Al is a potent deoxidation element used during the steel making process. Excess Al addition above 0.02% can induce AlN formation, thereby reducing the amount of strengthening MX (M being: Nb, V and X being: C, N) nitride precipitates in steel and consequently the creep strength properties.

(7) Cr: 10.5 to 12.00%,

[0036] Cr forms carbides that form at boundaries of the martensitic microstructure. Chromium carbides are essential for stabilization of the martensitic microstructure during exposure at elevated temperatures. Cr improves the high temperature oxidation behavior of steels. Contents of at least 10.5% are necessary to unfold the full oxidation improving effect of Cr additions. Cr contents above 12% result in increased δ-ferrite formation.

(8) Mo: 0.10 to 0.60%,

[0037] Mo is an important element for improvement of creep rupture strength that is also responsible for solid solution strengthening. This element is incorporated in carbides and intermetallic phases as well. Mo content of 0.10 % may be added. The Mo additions above 0.60 % will deteriorate toughness and induce increase of δ-ferrite content. Note that M and W contents shall satisfy the relationship (in weight %) $1 \leq Mo+0.5 \times W \leq 1.5$, in order to ensure the sufficient precipitation of carbides and intermetallic phases.

(9) V: 0.15 to 0.30%,

[0038] V combines with N to form coherent MX nitrides (M being : Nb, V and X being : C, N), which contribute to enhancement of long-term creep properties. Contents below 0.15% are not sufficient to achieve this long-term creep improving property effect while contents above 0.30% decrease the toughness and increase the danger for δ-ferrite contents above 5% in average volume.

(10) Ni: 0.10 to 0.40%,

[0039] Ni is an important toughness improving element. Therefore, a minimum content of 0.10 % is necessary. However, it reduces A_{c1} temperature and tends to reduce the creep rupture strength, if added in contents above 0.40 %. (11) B: 0.008 to 0.015%,

[0040] B is a decisive element responsible for stabilization of $M_{23}C_6$ carbides and delay of recovery of the martensitic microstructure. It strengthens the grain boundaries and improves the long-term stability of creep rupture strength. In addition, B is responsible for remarkable improvement of creep rupture ductility. For achievement of maximum strengthening effect additions of at least 0.008% are necessary. Contents above 0.015%, however, reduce substantially the maximum processing temperature of steels and are regarded as detrimental. B and N additions shall satisfy the relationship B/N≤1.5 to enable transformation using known hot-working processes. Indeed, this B/N relationship allows the fabrication of small or large diameter seamless and welded tubes, pipes and plates using manufacturing process according to the invention. Preferably, the B content should be between 0.0095 and 0.0130 (wt %).

(12) N: 0.002 to 0.020%,

[0041] Nitrogen is necessary for formation of MX (M being: Nb, V and X being: C, N) nitrides and carbonitrides responsible for achievement of creep rupture strength. At least 0.002% may be added. Excessive N additions i.e. above 0.020%, however, result in enhanced BN formation, thereby reducing the strengthening effect of B additions.

[0042] Preferably, B and N contents (in weight %) shall satisfy the following relationship:

$$B - \left({}^{11}/_{14}\right)\left(N - 10^{-(1/2.45)\cdot(logB+6.81)} - \left({}^{14}/_{48}\right)\cdot Ti\right) \geq 0.007$$

(13) Co: 1.50 to 3.00%,

[0043] Co is a very effective austenite forming element and useful in limiting δ-ferrite formation. Moreover, it has only a weak effect on A_{c1} temperature. Additionally, it is an element that improves creep strength properties by reducing the size of initial precipitates after heat treatment. Therefore, a minimum content of 1.50% shall be added. However, Co in excessive additions may induce embrittlement due to enhanced precipitaton of intermetallic phases during high temperature operation. At the same time Co is very expensive. Hence, a limitation of additions to 3.00%, preferably to 2.50%, is necessary.

[0044] It is preferable that the Ni, Co, Mn, C and N contents (in weight %) are in accordance with the following equation: $2.6 \leq 4 \cdot (Ni + Co + 0.5 \cdot Mn) - 20 \cdot (C + N) \leq 11.2$.

(14) W: 1.50 to 2.50%,

[0045] W is known as an effective solution strengthener. At the same time it is incorporated in carbides and forms C14 Laves phase, which may contribute to creep strength enhancement as well. Therefore, a minimum content of 1.50% is needed. However, this element is expensive, strongly segregating during steel making and casting process and it forms intermetallic phases that lead to significant embrittlement. Hence, the upper limit for W additions may be set to 2.50%. Note that Mo and W contents (in weight %) shall satisfy the relationship $1.00 \leq Mo+0.5W \leq 1.50$ in order to ensure the sufficient precipitation of carbides and intermetallic phases.(15) Nb: 0.02 to 0.07%.

[0046] Nb forms stable MX carbonitrides important not only for creep properties but also austenite grain size control. A minimum content of 0.02% may be added. Nb contents above 0.07% result in formation of coarse Nb carbides that may reduce the creep strength properties. Therefore the upper limit is set to 0.07%.

(16) Ti: 0.001-0.020%

[0047] Ti is a strong nitride forming element. It is helpful to protect free B by forming nitrides. Minimum content of 0.001% is needed for this purpose. Excessive Ti content above 0.020%, however, can reduce toughness properties due to formation of large blocky TiN precipitates.

[0048] The balance of the steel comprises iron and ordinary residual elements coming from steel making and casting process. By impurities we mean elements such as tantalum, zirconium and any other elements that can't be avoided. It is to be mentioned that Tantalum and zirconium are not intentionally added to the steel, however may be present in less than 50 ppm overall as unavoidable impurities.

[0049] In an embodiment of the steel, the unavoidable impurities may comprise one or more of copper (Cu), Arsenic (As), tin (Sn), antimony (Sb) and lead (Pb).

[0050] Cu may be present in a content equal or less than 0.20 %.

[0051] Element As may be present in a content equal or less than 150 ppm; Sn may be present in a content equal or less than 150 ppm; Sb may be present in a content equal or less than 50 ppm; Pb may be present in a content equal or less than 50 ppm and the total content As + Sn + Sb + Pb is equal or less than 0.04 % in mass.

[0052] The steel is normalized for a period of about 10 to about 120 minutes in the temperature range between 1050 °C and 1170°C and cooled down in air or water to room temperature, and then tempered for at least one hour in the temperature range between 750°C and 820°C.

[0053] It has been found out that the resulting steel possesses remarkable and absolutely excellent elevated temperature strength and superior steam-oxidation resistance. Moreover, it was found that by $Cr_{eq.}/Ni_{eq.}$ ratio being less than 2.3, the average δ-ferrite content can be limited to less than 5 vol.% to avoid toughness issues, wherein $Cr_{eq.}$ and $Ni_{eq.}$ are defined as Cr+6Si+4Mo+1.5W+11V+5Nb+8Ti and 40C+30N+2Mn+4Ni+2Co+Cu, respectively. Surprisingly, it was found that the B/N ratio equal or less than 1.5 has to be kept in order to enable the hot-working operation with known transformation processes.

[0054] The delta ferrite content shall not exceed 5 vol.-% since contents above 5vol.-% will impair the toughness properties.

[0055] By hot forming processes, it is meant: hot rolling, pilgering, hot drawing, forging, plug mill, push-bench process where the mandrel rod pushes the elongated hollow through several in-line roll stands to produce a hollow, continuous rolling, and other rolling processes known.

EXAMPLES

[0056] The benefits of the steel of the present invention will be explained in more detail on the basis of the following examples. Steels in accordance with the present invention (Steel 1, Steel 2) and also comparative example steels (Steel 3, Steel 4), having the chemical composition indicated in Table 1, have been cast to 100 kg ingots using vacuum induction melting furnace, then hot-rolled to plates (13-25mm thickness) and subsequently normalized and tempered. The normalizing heat-treatment was performed in the temperature range of 1060°C to 1100°C for 30 minutes, followed by air cooling to room temperature. The tempering was done at 780°C for 120 minutes, again followed by cooling in air.

[0057] Comparative example steels 3 and 4 have B contents below 0.008 and are therefore not in accordance with the invention.

[0058] In case of steel 3, the Ni, Co, Mn, C and N additions do not comply with equation

$$2.6 \leq 4 \cdot (Ni + Co + 0.5 \cdot Mn) - 20 \cdot (C + N) \leq 11.2 \text{ (in wt.-\%).}$$

[0059] The steel 4 does not fulfill the following formula:

$$B - (^{11}/_{14})(N - 10^{-(1/2.45)\cdot(logB+6.81)} - (^{14}/_{48}) \cdot Ti) \geq 0.007 \text{ (in wt. \%) either.}$$

Table 1

Element	Steel 1 (wt.%)	Steel 2 (wt.%)	Steel 3* (wt.%)	Steel 4* (wt.%)
C	0.15	0.14	0.158	0.152
Si	0.39	0.51	0.49	0.39
Mn	0.3	0.63	0.42	0.35
P	0.001	0.014	0.005	0.001
S	0.002	0.002	0.001	0.002
Al	0.007	0.011	0.007	0.006
Cr	11.19	11.18	11.36	10.85
Mo	0.49	0.41	0.31	0.49
V	0.27	0.19	0.25	0.25
Ni	0.3	0.24	0.23	0.31
B	0.0145	0.0108	0.0040	0.0052
N	0.011	0.013	0.042	0.015
Co	1.77	1.81	0.88	1.72
W	1.91	1.51	1.46	1.95
Nb	0.048	0.035	0.038	0.043
Ti	0.001	0.003	0.001	0.001
***) Comparitive steels**				

[0060] For the two example steels (Steel 1, Steel 2) the results presented in table 2 were obtained at room temperature for tensile strength, yield stress, elongation, reduction of area and Charpy V notch impact energy.

Table 2

	Steel 1	Steel 2	P92
$R_{p0.2}$ (MPa)	653	629	540
R_m (MPA)	840	804.5	710
A_5 (%)	20.5	20.75	23
Z(%)	64	57	65
A_{viso} (J) - RT	72	39	140

[0061] Creep tests, performed in accordance to ISO DIN EN 204, on the specimens of the two example steels showed furthermore a remarkable improvement of the creep rupture strength. This is reflected in rupture times being at least three times more than that of state-of-the-art steels like P91, P91, VM12-SHC, P122 and X20CrMoV11-1 during long-term creep testing at 130MPa and 100MPa. The results are displayed in Table 3. Also the comparative example steels does not reach the creep rupture strength of the steels according to the invention.

Table 3

Steel grade	Rupture time in h at 650°C for stresses	
	130 MPa	100MPa
Steel 1	*6470*	*23844*
Steel 2	*1824*	*13867*
Steel 3	*not tested*	*5900*
Steel 4	*526*	*3354*
VM12-SHC	*517*	*2828*
P91*	*44*	*498*
P92*	*686*	*4682*
P122 (single phase)**	*533*	*4572*
X20CrMoV11-1*	*55*	*210*
***) Average values calculated from strength values indicated in ECCC data sheet **) K. Kimura et al.. Proc. of ASME PVP Conference (PVP2012), 2012, Toronto, Canada**		

[0062] Figure 1 shows the schematic of mass gain due to oxidation in water vapor atmosphere at elevated temperatures plotted versus chromium content. The basis for the construction of the schematic is the oxidation tests in water vapor atmosphere performed according to ISO 21608:2012.

[0063] In the figure 1, three regions displaying different steam oxidation behavior have been defined as follows:

(I.) Non-protective behavior for mass gain above 10mg/cm^2 after 5,000h

(II.) Intermediate behavior for mass gain in the range 5-10mg/cm^2

(III.) Protective behavior for mass gains below 5mg/cm^2.

[0064] Correspondingly, the classification of different high Cr martensitic heat-resistant steels with respect to oxidation behavior was performed in the table 4 below. Regions I, II and III correspond to mass gains as described in Figure 1. The two example steels clearly outperform P91, P92, P122 and X20CrMoV11-1 with respect to steam oxidation resistance. The invention exhibits behavior comparable to VM12-SHC.

Table 4

	Mass gain (mg/cm^2)	
Test temperature (°C)	**600°C**	**650°C**
VM12-SHC	**III**	**III**
P92	**I**	**I**
X20CrMoV11-1	**III**	**I**
P122 (single phase)	**III**	**II**
Invention	**III**	**III**

[0065] According to the invention it is possible to provide a high chromium martensitic heat-resistant steel with enhanced creep properties and steam oxidation resistance that can be used to produce tubes, forgings, pipes and plates operating at high temperature in the power generation, chemical and petrochemical industry.

Claims

1. Steel for high-temperature applications having the following chemical composition in weight percent:

C: 0.10 to 0.16%
Si: 0.20 to 0.60%
Mn: 0.30 to 0.80%
P ≤0.020%
S ≤0.010%
Al ≤0.020%
Cr: 10.50to 12.00%
Mo: 0.10 to 0.60%
V: 0.15 to 0.30%
Ni: 0.10 to 0.40%
B: 0.008 to 0.015%
N: 0.002 to 0.020%
Co: 1.50 to 3.00%
W: 1.50 to 2.50%
Nb: 0.02 to 0.07%.
Ti: 0.001 to 0.020%

the balance of said steel being iron and unavoidable impurities.

2. Steel according to claim 1 wherein: $^{B}/_{N} \leq 1.5$.

3. Steel according to claim 1 or 2 wherein, in wt %: 1.00% ≤ Mo+0.5W ≤ 1.50 %

4. Steel according to anyone of claims 1 to 3 wherein in wt %:

$$B - (^{11}/_{14})(N - 10^{-(1/2.45)\cdot(logB+6.81)} - (^{14}/_{48}) \cdot Ti) \geq 0.007$$

5. Steel according to anyone of claims 1 to 4 wherein, in wt.-%:

$$2.6 \leq 4 \cdot (Ni + Co + 0.5 \cdot Mn) - 20 \cdot (C + N) \leq 11.2$$

6. Steel according to anyone of claims 1 to 5 wherein the carbon content is between 0.13 and 0.16%.

7. Steel according to anyone of claims 1 to 6 wherein the Mo content is between 0.30 and 0.60%.

8. Steel according to anyone of claims 1 to 7 wherein the B content is between 0.0095 and 0.013%.

9. Steel according to anyone of claims 1 to 8 wherein the Ti content is between 0.001 and 0.005%.

10. Steel according to anyone of claims 1 to 9 wherein the microstructure comprises in average at least 95 % of tempered martensite, the balance being delta ferrite.

11. Steel according to anyone of claims 1 to 10 wherein the microstructure comprises in average at least 98 % of tempered martensite, the balance being delta ferrite.

12. Steel according to anyone of claims 1 to 11 wherein the microstructure is martensitic and free of delta ferrite.

13. Method of production of steel according to anyone of claims 1 to 9 comprising the following steps:

- casting a steel with a chemical composition according to anyone of claims 1 to X,

- hot forming said steel,
- heating said steel and holding said steel for a time between 10 and 120 minutes in the temperature range between 1050 °C and 1170°C,
- cooling said steel down to room temperature,
- reheating said steel and holding said steel up to a tempering temperature TT that is between 750°C and 820°C for at least one hour,
- cooling said steel down to room temperature.

14. Method of production of steel according to claim 13 wherein the cooling step is done using air cooling or water cooling.

15. Use of a steel according to anyone of claims 1 to 12 to produce a seamless or welded tube, pipe or plate.

16. Use of a method according to anyone of method claims 13 or 14 to produce a seamless or welded tube, pipe or plate.

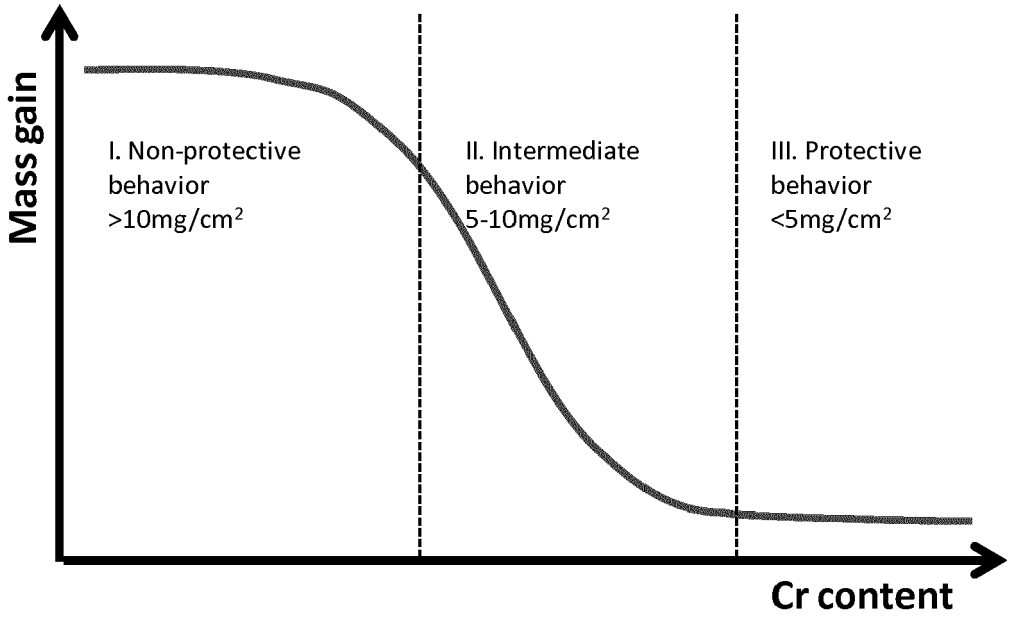

Mass gain
I. Non-protective behavior >10mg/cm2
II. Intermediate behavior 5-10mg/cm2
III. Protective behavior <5mg/cm2
Cr content

FIGURE 1

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EUROPEAN SEARCH REPORT

Application Number
EP 16 17 9114

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Place of search	Date of completion of the search	Examiner
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