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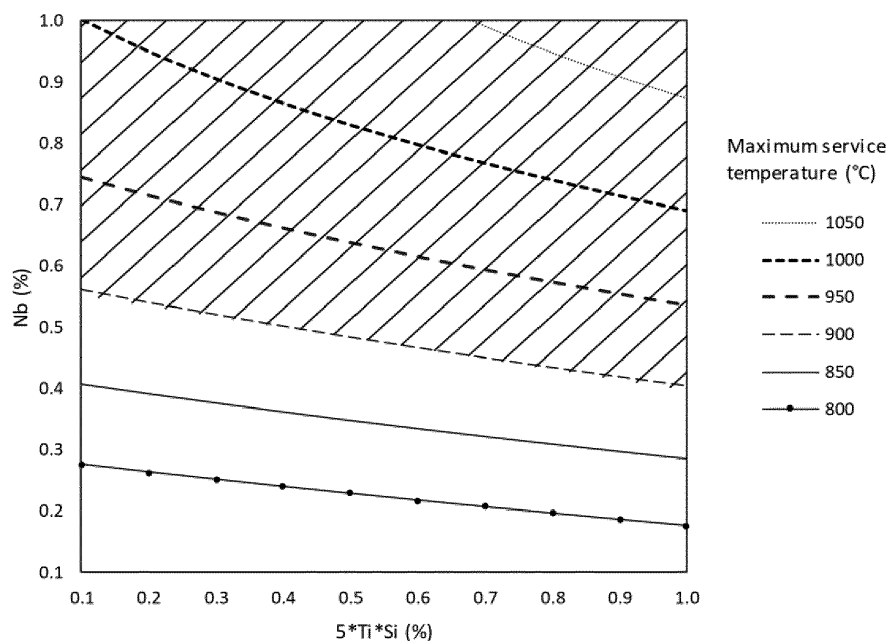
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(54) **FERRITIC STAINLESS STEEL**

(57) The invention relates to a Ferritic stainless steel having excellent corrosion and sheet forming properties. The steel consists of in weight percentages 0.003 - 0.035 % carbon, 0.05 - 1.0 % silicon, 0.10 - 0.8 % manganese, 18 - 24 % chromium, 0.05 - 0.8 % nickel, 0.003 - 2.5 % molybdenum, 0.2 - 0.8 % copper, 0.003 - 0.05 % nitrogen, 0.05 - 1.0 % titanium, 0.05 - 1.0 % niobium, 0.03 - 0.5 % vanadium, 0.010 - 0.04 % aluminium, and the sum C+N less than 0.06 %, the remainder being iron and inevitable

impurities, wherein the ratio  $(Ti+Nb)/(C+N)$  is higher or equal to 8, and less than 40, and the ratio  $Tieq/Ceq = (Ti + 0.515*Nb + 0.940*V)/(C+0.858*N)$  is higher or equal to 6, and less than 40, and  $Leq = 5.8*Nb + 5*Ti*Si$  is higher or equal to 3.3, and the steel is produced using AOD (Argon-Oxygen-Decarburization) technology.



**Fig. 1**

## Description

**[0001]** This invention relates to a stabilized ferritic stainless steel having good corrosion resistance, good weldability and enhanced high temperature strength for use in high temperature service in components used in applications such as automotive exhaust systems, fuel cells and other energy sector applications, appliances, furnaces and other industrial high temperature systems.

**[0002]** The most critical point in developing ferritic stainless steel is how to take care of carbon and nitrogen elements. These elements have to be bound to carbides, nitrides or carbonitrides. The elements used in this type of binding are called stabilizing elements. The common stabilizing elements are niobium and titanium. The requirements for stabilization of carbon and nitrogen can be diminished for ferritic stainless steels where for instance the carbon content is very low, less than 0.01 weight %. However, this low carbon content causes requirements for the manufacturing process. The common AOD (Argon-Oxygen-Decarburization) producing technology for stainless steels is not any more practical and, therefore, more expensive producing methods shall be used, such as the VOD (Vacuum-Oxygen-Decarburization) producing technology.

**[0003]** Intermetallic Laves phase particles, which may form in ferritic stainless steel, increase the high temperature strength of the steel provided that the particles remain small and stable in the operating temperatures. Additionally, Laves phase particles, precipitated inside grains and on grain boundaries, also inhibit grain growth. Alloying of a balanced combination of niobium, silicon and titanium in ferritic stainless steel promotes precipitation of intermetallic Laves phase and stabilizes the phase by increasing the dissolution temperature of precipitates.

**[0004]** The microstructure formed in the weld depends on the chemical composition of weld metal. When a sufficient amount of titanium is used in the stabilization of the interstitial elements carbon and nitrogen, the compounds formed during the stabilization, such as TiN, produce an equiaxed, fine grained structure in welds. The equiaxed, fine grained structure improves the ductility and toughness of the welds. Unwanted columnar grains can cause hot cracking as impurities may segregate to the weld centreline. Large columnar grains also decrease the toughness of the weld.

**[0005]** The EP patent EP2922978B describes ferritic stainless steel having excellent corrosion and sheet forming properties, characterized in that the steel consists of in weight percentages 0.003 - 0.035 % carbon, 0.05 - 1.0 % silicon, 0.1 - 0.8 % manganese, 20 - 21.5 % chromium, 0.05 - 0.8 % nickel, 0.003 - 0.5 % molybdenum, 0.2 - 0.8 % copper, 0.003 - 0.05 % nitrogen, 0.05 - 0.15 % titanium, 0.25% - 0.8 % niobium, 0.03 - 0.5 % vanadium, 0.010- 0.04 % aluminium, and the sum C+N less than 0.06 %, the remainder being iron and inevitable impurities, wherein the ratio  $(Ti+Nb)/(C+N)$  is higher or equal to 8, and less than 40, and the ratio  $Tieq/Ceq = (Ti + 0.515 \cdot Nb + 0.940 \cdot V)/(C + 0.858 \cdot N)$  is higher or equal to 6, and less than 40.

**[0006]** The EP patent 1818422 describes a niobium stabilized ferritic stainless steel having, among others, less than 0.03 weight % carbon, 18 - 22 weight % chromium, less than 0.03 weight % nitrogen and 0.2 - 1.0 weight % niobium. In accordance with this EP patent the stabilization of carbon and nitrogen is carried out using only niobium.

**[0007]** The EP patent application 2163658 describes a ferritic stainless steel with sulfate corrosion resistance containing less than 0.02 % carbon, 0.05-0.8 % silicon, less than 0.5 % manganese, 20-24 % chromium, less than 0.5 % nickel, 0.3-0.8 % copper, less than 0.02 % nitrogen, 0.20-0.55 % niobium, less than 0.1 % aluminium and the balance being iron and inevitable impurities. In this ferritic stainless only niobium is used in the stabilization of carbon and nitrogen.

**[0008]** The WO publication 2012046879 relates to a ferritic stainless steel to be used for a separator of a proton-exchange membrane fuel cell. A passivation film is formed on the surface of the stainless steel by immersing the stainless steel in a solution containing mainly hydrofluoric acid or a liquid mixture of hydrofluoric acid and nitric acid. The ferritic stainless steel contains carbon, silicon, manganese, aluminium, nitrogen, chromium and molybdenum in addition to iron as the necessary alloying elements. All other alloying elements described in the reference WO 2012046879 are optional. As described in the examples of this WO publication the ferritic stainless steel having a low carbon content is produced by vacuum smelting, which is a very expensive manufacturing method.

**[0009]** EP1083241 describes niobium stabilized ferritic chromium steel strip, produced from a steel having specified molybdenum, silicon and tin contents and containing a cubic iron-niobium phase as the sole intermetallic phase at high temperature. A niobium stabilized ferritic 14% chromium steel strip is produced from a steel of composition (by wt.)  $\leq$  0.02% C, 0.002-0.02% N, 0.05-1% Si, greater than 0 to 1% Mn, 0.2-0.6% Nb, 13.5-16.5% Cr, 0.02-1.5% Mo, greater than 0 to 1.5% Cu, greater than 0 to 0.2% Ni, greater than 0 to 0.020% P, greater than 0 to 0.003% S, greater than 0.005 to 0.04% Sn, balance Fe and impurities, the Nb, C and N contents satisfying the relationship  $Nb/(C + N) \geq 9.5$ , by: (a) reheating before hot rolling at 1150-1250 (preferably 1175) degrees C; (b) coiling at 600-800 (preferably 600) degrees C; (c) cold rolling, optionally after pre-annealing; and (d) final annealing at 800-1100 (preferably 1050) degrees C for 1-5 (preferably 2) min. An independent claim is also included for a niobium stabilized 14% chromium ferritic steel sheet obtained by the above process.

**[0010]** EP1170392 describes ferritic stainless steel comprising all three of Co, V, and B, having a Co content of about 0.01 mass% to about 0.3 mass%, a V content of about 0.01 mass% to about 0.3 mass%, and a B content of about 0.0002 mass% to about 0.0050 mass%, and having superior secondary working embrittlement resistance and superior

high temperature fatigue characteristics. Further components are (in mass%): 0.02% or less of C, 0.2 to 1.0% Si, 0.1 to 1.5% Mn, 0.04% or less of P, 0.01% or less of S, 11.0 to 20.0% of Cr, 0.1 to 1.0% Ni, 1.0 to 2.0% Mo, 1.0% or less of Al, 0.2 to 0.8% of Nb, 0.02% or less of N and optionally 0.05 to 0.5% Ti, Zr or Ta, 0.1 to 2.0% Cu, 0.05 to 1.0% W, 0.001 to 0.1% Mg and 0.0005 to 0.005% Ca.

**[0011]** US patent 4726853 concerns a strip or sheet of ferritic stainless steel, usually in the annealed state, the final annealing operation then being followed in most cases by a finishing and cold-working pass or "skin pass", producing a degree of elongation of less than 1%, intended in particular for the production of exhaust pipes and manifolds. The composition of the strip or sheet is as follows (% by weight):

(C+N)<0.060-Si<0.9-Mn<1

Cr 15 to 19-Mo<1-Ni<0.5-Ti<0.1-Cu<0.4-S<0.02-P<0.045

Zr=0.10 to 0.50 with Zr between  $7(C+N)-0.1$  and  $7(C+N)+0.2$  Nb between 0.25 and 0.55 if  $Zr \geq 7(C+N)$  and between  $0.25+7(C+N)-Zr$  and  $0.55+7(C+N)-Zr$  if  $Zr < 7(C+N)$

Al 0.020 to 0.080; other elements and Fe: balance.

**[0012]** EP0478790 describes a heat-resistant ferritic stainless steel improved in low-temperature toughness, prevented from undergoing high-temperature weld cracking, and useful as a material of a passage of automobile exhaust gas, particularly a passage exposed to high temperature between an engine and a converter, which steel comprises up to 0.03 % of carbon, 0.1 to 0.8 % of silicon, 0.6 to 2.0 % of manganese, up to 0.006 % of sulfur, up to 4 % of nickel, 17.0 to 25.0 % of chromium, 0.2 to 0.8 % of niobium, 1.0 to 4.5 % of molybdenum, 0.1 to 2.5 % of copper, up to 0.03 % of nitrogen, and optionally a necessary amount of at least one of aluminum, titanium, vanadium, zirconium, tungsten, boron and REM, wherein the manganese to sulfur ratio is 200 or above,  $[Nb] = Nb \% - 8(C \% + N \%) \geq 0.2$ , and  $Ni \% + Cu \% \leq 4$ , the balance being iron and inevitable impurities in the production process.

**[0013]** EP2557189 describes ferritic stainless steel sheet for an exhaust part which has little deterioration in strength even if undergoing long term heat history and is low in cost, excellent in heat resistance and workability characterized by containing, characterized by containing, by mass%, C: less than 0.010%, N: 0.020% or less, Si: over 0.1% to 2.0%, Mn: 2.0% or less, Cr: 12.0 to 25.0%, Cu: over 0.9 to 2%, Ti: 0.05 to 0.3%, Nb: 0.001 to 0.1%, Al: 1.0% or less, and B: 0.0003 to 0.003%, having a Cu/(Ti+Nb) of 5 or more, and having a balance of Fe and unavoidable impurities.

**[0014]** The object of the present invention is to eliminate some drawbacks of the prior art and to achieve a ferritic stainless steel having good corrosion resistance, improved weldability and enhanced high temperature strength, which steel is stabilized by niobium, titanium and vanadium and is produced using AOD (Argon-Oxygen-Decarburization) technology. The essential features of the present invention are enlisted in the appended claims.

**[0015]** The chemical composition of the ferritic stainless steel according to the invention consists of in weight % 0.003 - 0.035 % carbon, 0.05 - 1.0 % silicon, 0.10 - 0.8 % manganese, 18 - 24 % chromium, 0.05 - 0.8 % nickel, 0.003 - 2.5 % molybdenum, 0.2 - 0.8 % copper, 0.003 - 0.05 % nitrogen, 0.05 - 1.0 % titanium, 0.05 - 1.0 % niobium, 0.03 - 0.5 % vanadium, 0.01 - 0.04 % aluminium, and the sum C+N less than 0.06 %, the rest being iron and evitable impurities occupying in stainless steels, in such conditions that the sum of (C+N) is less than 0.06 % and the ratio (Ti+Nb)/(C+N) is higher or equal to 8, and less than 40, and the ratio  $(Ti + 0.515 \cdot Nb + 0.940 \cdot V)/(C + 0.858 \cdot N)$  is higher or equal to 6, and less than 40, and  $5.8 \cdot Nb + 5 \cdot Ti \cdot Si$  is higher or equal to 3.3. The ferritic stainless steel according to the invention is produced using AOD (Argon-Oxygen-Decarburization) technology.

**[0016]** The effects and the content, in weight % if nothing else mentioned, of each alloying element are discussed in the following:

Carbon (C) decreases elongation and r-value and, preferably, carbon is removed as much as possible during the steel making process. The solid-solution carbon is fixed as carbides by titanium, niobium and vanadium as described below. The carbon content is limited to 0.035 %, preferably to 0.03 %, but having at least of 0.003 % carbon.

**[0017]** Silicon (Si) is used to reduce chromium from slag back to melt. Some silicon remainders in steel are necessary to make sure that reduction is done well. In the solid solution, silicon boosts formation of Laves phases and stabilizes Laves phase particles at higher temperatures. Therefore, the silicon content is less than 1.0 %, but at least 0.05 %.

**[0018]** Manganese (Mn) degrades the corrosion resistance of ferritic stainless steel by forming manganese sulphides. With low sulphur (S) content the manganese content is less than 0.8 %, preferable less than 0.65 %, but at least 0.10 %.

**[0019]** Chromium (Cr) enhances oxidation resistance and corrosion resistance. In order to achieve corrosion resistance comparable to steel grade EN 1.4301, the chromium content must be 18 - 24 %, preferably 20 - 22 %.

**[0020]** Nickel (Ni) is an element favourably contributing to the improvement of toughness, but nickel has sensitivity to stress corrosion cracking (SCC). In order to consider these effects the nickel content is less than 0.8 %, preferably less than 0.5 % so that the nickel content is at least 0.05 %.

**[0021]** Molybdenum (Mo) enhances corrosion resistance but reduces elongation to fracture. The molybdenum content is less than 2.5 %, but at least 0.003%. For applications in highly corrosive environments with low acidic pH-values  $\leq 4$ ,

the molybdenum content is preferably less than 2.5% but at least 0.5%. For applications in less corrosive environments with neutral or high pH-values >4, the more preferable range is 0.003% - 0.5% molybdenum.

**[0022]** Copper (Cu) improves corrosion resistance in acidic solutions, but high copper content can be harmful. The copper content is thus less than 0.8 %, preferably less than 0.5 %, but at least 0.2 %.

**[0023]** Nitrogen (N) reduces elongation to fracture. The nitrogen content is less than 0.05 %, preferably less than 0.03 %, but at least 0.003 %.

**[0024]** Aluminium (Al) is used to remove oxygen from melt. The aluminium content is less than 0.04 %.

**[0025]** Titanium (Ti) is very useful because it forms titanium nitrides with nitrogen at very high temperatures. Titanium nitrides prevent grain growth during annealing and welding. In welds, titanium alloying promotes the formation of equiaxed, fine grained structure. Titanium is the cheapest element of chosen stabilization elements titanium, vanadium and niobium. Therefore, using titanium for stabilization is an economic choice. The titanium content is less than 1.0 %, but at least 0.05 %. The more preferable range is 0.07% - 0.40% titanium.

**[0026]** Niobium (Nb) is used to some extent to bind carbon to niobium carbides. With niobium the recrystallization temperature can be controlled. Niobium stimulates precipitation of Laves phases particles and has positive effect their stability at high temperatures. Niobium is the most expensive element of chosen stabilization elements titanium, vanadium and niobium. The niobium content is less than 1.0 %, but at least 0.05 %.

**[0027]** Vanadium (V) forms carbides and nitrides at lower temperatures. These precipitations are small and major part of them is usually inside grains. Amount of vanadium needed to carbon stabilization is only about half of amount of niobium needed to same carbon stabilization. This is because vanadium atomic weight is only about a half of niobium atomic weight. Vanadium is economic choice for stabilization element since vanadium is cheaper than niobium. Vanadium also improves toughness of steel. The vanadium content is less than 0.5 %, but at least 0.03 % preferably 0.03 - 0.20 %.

**[0028]** The invention is described below in further detail with reference to the attached drawings, of which

Figure 1 is a graph showing the combination of Ti, Nb and Si content, resulting in enhanced high temperature mechanical properties in a material according to the present invention,

Figure 2 is a micrograph showing a typical microstructure used for determining the chemical composition of Laves phase particles by energy dispersive spectrometry (EDS),

Figure 3 is a micrograph showing a coarse-grained, columnar structure formed in the weld in autogenous welding when the steel does not have a sufficient amount of titanium, (a) cross-section transverse to the weld, and (b) cross-section in the plane of welded sheet, and

Figure 4 is a micrograph of a fine-grained, equiaxed structure formed in the weld in autogenous welding when the steel has a sufficient amount of titanium.

**[0029]** Using all three stabilization elements, titanium, niobium and vanadium in the ferritic stainless steel according to the invention, it is possible to achieve an atomic lattice which is practically interstitially free. That means that essentially all carbon and nitrogen atoms are bound with stabilization elements. When a sufficient amount of titanium is used in the stabilization of the interstitial elements carbon and nitrogen, the compounds formed during the stabilization, such as TiN, promote formation of equiaxed and fine grain structure in welds. The equiaxed, fine grained structure improves the ductility and toughness of welds. A sufficient titanium content therefore prevents forming coarse columnar structure in welds. Columnar grains can cause hot cracking as impurities could segregate to the weld centreline. Large columnar grains can also decrease the toughness of the weld. Using additionally sufficient Ti, Si and Nb content, it is possible to achieve ferritic stainless steel with enhanced mechanical properties at high temperatures. The combinations of Ti, Nb and Si contents resulting in enhanced high temperature mechanical properties in the present invention are shown in figure 1. The region is determined by having  $5.8 \cdot \text{Nb} + 5 \cdot \text{Ti} \cdot \text{Si}$  greater than or equal to 3.3.

**[0030]** Several stainless steel alloys were prepared for testing the ferritic stainless steel of the invention. During the preparation every alloy was melted, cast and hot-rolled. The hot-rolled plate was further annealed and pickled before cold-rolling. Then the cold-rolled sheet at the final thickness was again annealed and pickled. The table 1 further contains the chemical compositions of the reference materials EN 1.4509 and EN 1.4622.

Alloy	C	Si	Mn	P	S	Cr	Ni	Mo	Ti	Nb	Cu	V	Al	N
A	0.018	0.41	0.34	0.03	0.001	20.9	0.2	0.0	0.22	0.62	0.41	0.05	0.03	0.02
B	0.021	0.43	0.33	0.03	0.001	20.9	0.2	0.0	0.25	0.78	0.38	0.05	0.03	0.02
C	0.021	0.59	0.32	0.03	0.001	20.7	0.2	0.0	0.27	0.78	0.38	0.06	0.04	0.02

(continued)

Alloy	C	Si	Mn	P	S	Cr	Ni	Mo	Ti	Nb	Cu	V	Al	N
D	0.020	0.75	0.33	0.03	0.001	20.8	0.2	0.0	0.27	0.78	0.38	0.06	0.03	0.02
E	0.024	0.71	0.32	0.03	0.001	21.0	0.2	0.0	0.20	0.81	0.41	0.05	0.03	0.02
F	0.020	0.58	0.32	0.03	0.001	20.9	0.2	0.0	0.19	0.96	0.39	0.06	0.03	0.02
G	0.019	0.59	0.31	0.03	0.001	20.8	0.2	1.0	0.22	0.81	0.39	0.06	0.03	0.02
H	0.020	0.59	0.30	0.03	0.001	20.9	0.2	2.0	0.20	0.79	0.38	0.06	0.03	0.02
EN 1.4509	0.015	0.5	0.5	0.03	0.001	18.0	0.2	0	0.12	0.4	0.2	0	0	0.02
EN 1.4622	0.015	0.5	0.4	0.03	0.001	20.8	0.2	0	0.17	0.4	0.4	0.07	0	0.02

Table 1: Chemical compositions

**[0031]** From table 1 it is seen that the alloy A has smaller amount of niobium and silicon compared to the other alloys from B to H. The alloys B, C and D have the same amount of niobium, while the amount of silicon is increasing gradually from the alloy B to C and to alloy D. The alloy E has essentially the same chemical composition as the alloy D except for small variations in the amounts of silicon, titanium and niobium. The alloy F has essentially the same amount of silicon as the alloy C, while the niobium content of alloy F is the highest among all alloys from A to H. The alloys G and H contain also molybdenum in addition to silicon, titanium and niobium. All alloys A - H are triple stabilized with titanium, niobium and vanadium in accordance with the invention.

**[0032]** When using niobium, titanium and vanadium in the stabilization of the interstitial elements carbon and nitrogen in the ferritic stainless steel of the invention, the compounds which are generated during the stabilization, are such as titanium carbide (TiC), titanium nitride (TiN), niobium carbide (NbC), niobium nitride (NbN), vanadium carbide (VC) and vanadium nitride (VN). In this stabilization a simple formula is used to evaluate the amount and the effect of stabilization as well as the role of the different stabilization elements.

**[0033]** The connection between the stabilization elements titanium, niobium and vanadium is defined by a formula (1) for a stabilization equivalent ( $Ti_{eq}$ ) where the content of each element is in weight %:

$$Ti_{eq} = Ti + 0.515 \cdot Nb + 0.940 \cdot V \quad (1)$$

**[0034]** Respectively, the connection between of the interstitial elements carbon and nitrogen is defined by a formula (2) for an interstitial equivalent ( $C_{eq}$ ) where the contents of carbon and nitrogen are in weight %:

$$C_{eq} = C + 0.858 \cdot N \quad (2)$$

**[0035]** The ratio  $Ti_{eq}/C_{eq}$  is used as one factor for determining the disposition for sensitization, and the ratio  $Ti_{eq}/C_{eq}$  is higher or equal to 6 and the ratio  $(Ti+Nb)/(C+N)$  higher or equal to 8 for the ferritic stainless steel of the invention in order to avoid the sensitization. The EP patent EP292278B gives additional information regarding sensitization to grain boundary corrosion. In this document it is shown that stabilization against intergranular corrosion is successful if  $Ti_{eq}/C_{eq}$  is higher or equal to 6 and  $(Ti+Nb)/(C+N)$  higher or equal to 8.

**[0036]** The enhanced high temperature strength of invented steel is ensured by fine dispersion of thermodynamically stable Laves phase particles. The alloying of Nb, Ti and Si must be carefully balanced in order to obtain an optimal microstructure for high service temperatures. The correct alloying promotes precipitation of Laves phase particles and raises their dissolution temperature. The Laves phase particles are formed quickly in exposure to temperatures in the range from 650 to 850°C. Figure 2 illustrates intergranular and intragranular precipitates observed in the alloys A to H when the material was exposed to the temperature of 800°C for 30 minutes. Chemical composition of precipitated particles was determined by means of by energy dispersive spectrometry (EDS). The results in table 2 reveal that particles formed in the steel of invention are Laves phase precipitates. According to table 2, the chemical composition of precipitated particles in the steel of invention follows the model  $A_2B$ , where A is a combination of Fe and of Cr and B is a combination of Nb, Si and Ti. According to EDS measurements given in table 2, the chemical formula of the Laves phase particles is  $(Fe_{0.8}Cr_{0.2})_2(Nb_{0.70}Si_{0.25}Ti_{0.05})$ . The number of Fe, Cr, Nb, Si and Ti atoms in the molecule depend on alloying and on heat cycles experienced by the material.

Table 2: Chemical composition of 10 Laves phase particles in the steel of the invention according to energy dispersive spectrometry (EDS).

EDS chemical composition (at.%)					
Analysis point	Fe	Nb	Cr	Si	Ti
1	52.6	24.9	10.6	8.9	1.5
2	52.3	25.1	10.5	8.9	1.6
3	53.5	23.8	11.1	8.6	1.5
4	52.7	24.8	10.6	8.8	1.6
5	52.6	23.0	10.5	8.6	1.5
6	52.9	24.8	10.6	8.8	1.5
7	53.0	24.5	10.7	8.7	1.7
8	53.0	24.3	10.9	8.8	1.6
9	52.3	24.5	10.8	8.8	1.8
10	52.7	24.5	10.7	9.0	1.7
Average	52.8	24.4	10.7	8.8	1.6

**[0037]** A balanced combination of silicon, niobium and titanium ensures that the steel contains sufficient amount Laves phase particles in high service temperatures above 900°C. The connection between the Laves phase forming elements titanium, niobium and silicon is defined by a formula (3) for a Laves phase equivalent number  $L_{eq}$  where the content of each element is in weight %:

$$L_{eq} = 5.8 \cdot Nb + 5 \cdot Ti \cdot Si \quad (3)$$

**[0038]** The Laves phase equivalent number  $L_{eq}$  is higher or equal to 3.3 for the ferritic stainless steel of the invention in order to guarantee enhanced high temperature strength properties. Laves phase equivalent corresponds to the lower boundary of the region indicated order to guarantee enhanced high temperature strength properties. For higher service temperatures above 950°C, Laves phase equivalent number  $L_{eq}$  is higher or equal to 4.5.

**[0039]** The values for ratios  $Ti_{eq}/C_{eq}$ ,  $(Ti+Nb)/(C+N)$  and the value of equivalent  $L_{eq}$  are calculated in table 3 for the alloys A to H. The values of table 3 show that the alloys A - H and the reference materials have favourable values for both the ratios  $Ti_{eq}/C_{eq}$  and  $(Ti+Nb)/(C+N)$ . Instead, only the alloys A - H, have favourable values for the Laves phase equivalent number  $L_{eq}$  in accordance with the invention.

Table 3: Values for the ratios  $Ti_{eq}/C_{eq}$ ,  $(Ti+Nb)/(C+N)$  and the Laves phase equivalent number  $L_{eq}$ .

	Alloy	$Ti_{eq}/C_{eq}$	$(Ti+Nb)/(C+N)$	$L_{eq}$
Invention	A	16.6	22.0	4.0
	B	18.6	25.6	5.1
	C	19.3	25.9	5.3
	D	20.2	27.1	5.5
	E	16.0	22.8	5.5
	F	20.0	28.9	6.1
	G	20.0	27.7	5.3
	H	19.3	27.0	5.2
Reference	EN 1.4509	10.1	14.9	<u>2.3</u>
	EN 1.4622	11.7	16.3	<u>2.3</u>

**[0040]** The dissolution of precipitated Laves phase determines the upper limit for the service temperature for the ferritic stainless steels of the invention. The dissolution temperature was calculated using thermodynamic simulation software Thermo-Calc version 2018b for the alloys of table 1. The results are presented in table 4. The values for the dissolution temperature are favourable and above the target service temperature of 900°C for the alloys A - H. The dissolution temperatures are unfavourably below the target temperature of 900°C for the reference materials.

Table 4: The temperature at which the strengthening Laves phase particles dissolve under sustained exposure. A value above T=900°C is considered satisfactory.

	Alloy	Tsol (°C)
Invention	A	929
	B	986
	C	1003
	D	1013
	E	1009
	F	1039
	G	1009
	H	1009
Reference	EN 1.4509	<u>849</u>
	EN 1.4622	<u>839</u>

**[0041]** The elevated temperature tensile strength of all alloys listed in the table 1 was determined according to the elevated temperature tensile testing standard EN ISO 10002-5. The results for tests performed at T=950°C and T=1000°C are presented in table 5.

Table 5: The tensile strength measured according to EN ISO 12002-5. Rm value above 30 MPa at 950°C and above 20 MPa at 1000°C is considered satisfactory.

	Alloy	Rm at 950°C (MPa)	Rm at 1000°C (MPa)
Invention	A	31	25
	B	34	26
	C	32	27
	D	33	26
	E	31	22
	F	31	28
	G	41	32
	H	47	36
Reference	EN 1.4509	<u>26</u>	<u>18</u>
	EN 1.4622	<u>24</u>	<u>18</u>

**[0042]** The mechanical strength Rm is considered insufficient when Rm < 30MPa at 950°C or Rm < 20 MPa at 1000°C. The results in the table 5 show that the steels in accordance with the invention satisfy these requirements whereas the reference materials EN 1.4509 and EN 1.4622 do not satisfy these requirements.

**[0043]** As corrosion resistance is the most important property of stainless steel, the pitting corrosion potential of all the alloys listed in the table 1 was determined potentiodynamically. The alloys were wet ground with 320 mesh and allowed to repassivate in air at ambient temperature for at least 24 hours. The pitting potential measurements were done in naturally aerated aqueous 1.2 wt-% NaCl-solution (0.7 wt-% Cl<sup>-</sup>, 0.2 M NaCl) at room temperature of about 22°C. The polarization curves were recorded at 20 mV/min using crevice-free flushed-port cells (Avesta cells as described in ASTM G150) with an electrochemically active area of about 1 cm<sup>2</sup>. Platinum foils served as counter electrodes. KCl

saturated calomel electrodes (SCE) were used as reference electrodes. The average value of six breakthrough pitting potential measurements for each alloy was calculated and is listed in table 2.

[0044] The results in table 6 show that the ferritic stainless steel of the invention has better pitting corrosion potential than the reference steel EN 1.4509. The pitting corrosion potential of the alloys A - F is essentially in the same with the reference steel EN 1.4622, whereas the pitting corrosion potential of Mo-alloyed alloys G and H is superior to that of the reference material EN 1.4622.

Table 6: Pitting corrosion potential for the alloys A - H and for the reference materials.

	Alloy	Corrosion potential (mV)
Invention	A	428
	B	452
	C	465
	D	484
	E	465
	F	486
	G	659
	H	1000
Reference	EN 1.4509	303
	EN 1.4622	411

[0045] The equiaxial, fine grained structure of welds is ensured if a sufficient amount of titanium is used for stabilization. The compounds formed by titanium in the liquid weld metal, such as TiN, act as nucleation sites for heterogenous solidification resulting in equiaxed, fine grained structure in welds. The other elements used for stabilization, vanadium and niobium, do not form compounds that will act as nucleation sites in the liquid metal. Therefore, a coarse-grained weld with columnar grain structure results if the amount of titanium is not sufficiently high enough. The coarse-grained, columnar structure can cause hot cracking as impurities may segregate to the weld centreline. Large columnar grains also decrease the toughness of the weld. The problem is particularly serious in autogenous welding, where the chemical composition of weld metal cannot be changed by the welding additives. The influence of the stabilization method on the weld structure is well-known and is discussed in detail for example in the journal article published by W. Gordon and A. Van Bennecom (W. Gordon & A. van Bennekom. Review of stabilisation of ferritic stainless steels. Materials Science and Technology, 1996. Vol. 12, no. 2, pp. 126-131).

[0046] Figure 3 shows an illustrative example of coarse-grained, columnar weld structure obtained in autogenous welding when insufficient amount of titanium is alloyed in the steel. Figure 4 shows an example of fine-grained, equiaxial weld structure obtained in autogenous welding when sufficient amount of titanium was alloyed in the steel. The alloys A-H according to the invention and the reference materials EN 1.4509 and 1.4622 have favourable amount of titanium in order to produce fine-grained equiaxial weld structure in autogenous welding.

## Claims

1. Ferritic stainless steel having excellent corrosion and sheet forming properties, **characterized in that** the steel consists of in weight percentages 0.003 - 0.035 % carbon, 0.05 - 1.0 % silicon, 0.10 - 0.8 % manganese, 18 - 24 % chromium, 0.05 - 0.8 % nickel, 0.003 - 2.5 % molybdenum, 0.2 - 0.8 % copper, 0.003 - 0.05 % nitrogen, 0.05 - 1.0 % titanium, 0.05 - 1.0 % niobium, 0.03 - 0.5 % vanadium, 0.010 - 0.04 % aluminium, and the sum C+N less than 0.06 %, the remainder being iron and inevitable impurities, wherein the ratio (Ti+Nb)/(C+N) is higher or equal to 8, and less than 40, and the ratio  $Ti_{eq}/C_{eq} = (Ti + 0.515 \cdot Nb + 0.940 \cdot V)/(C + 0.858 \cdot N)$  is higher or equal to 6, and less than 40, and  $L_{eq} = 5.8 \cdot Nb + 5 \cdot Ti \cdot Si$  is higher or equal to 3.3, and the steel is produced using AOD (Argon-Oxygen-Decarburization) technology.
2. Ferritic stainless according to the claim 1, **characterized in that** the carbon content is less than 0.03 weight %, but



at least 0.003 %.

3. Ferritic stainless steel, according to any of the preceding claims, **characterized in that** the manganese content is 0.10 - 0.65 %.
4. Ferritic stainless steel, according to any of the preceding claims, **characterized in that** the chromium content is less than 22.0 weight %, but at least 20.0 %.
5. Ferritic stainless steel, according to any of the preceding claims, **characterized in that** the nickel content is less than 0.5 weight %, but at least 0.05 %.
6. Ferritic stainless steel, according to any of the preceding claims, **characterized in that** the molybdenum content is 0.003 - 0.5 weight % in corrosive environments with neutral or high pH-values >4.
7. Ferritic stainless steel, according to any of the preceding claims, **characterized in that** the molybdenum content is 0.5 - 2.5 weight % in highly corrosive environments with low acidic pH-values  $\leq 4$ .
8. Ferritic stainless steel, according to any of the preceding claims, **characterized in that** the copper content is less than 0.5 weight %, but at least 0.2%.
9. Ferritic stainless steel, according to any of the preceding claims, **characterized in that** the nitrogen content is less than 0.03 weight %, but at least 0.003 %.
10. Ferritic stainless steel, according to any of the preceding claims, **characterized in that** the titanium content is 0.07 - 0.40 weight %.
11. Ferritic stainless steel, according to any of the preceding claims, **characterized in that** the vanadium content is 0.03 - 0.20 weight %.
12. Ferritic stainless steel, according to any of the preceding claims, **characterized in that** the ratio  $(\text{Ti}+\text{Nb})/(\text{C}+\text{N})$  is higher or equal to 20, and less than 30.
13. Ferritic stainless steel, according to any of the preceding claims, **characterized in that** the ratio  $\text{Ti}_{\text{eq}}/\text{C}_{\text{eq}} = (\text{Ti} + 0.515 \cdot \text{Nb} + 0.940 \cdot \text{V})/(\text{C} + 0.858 \cdot \text{N})$  is higher or equal to 15, and less than 30.
14. Ferritic stainless steel, according to any of the preceding claims, **characterized in that** the  $\text{L}_{\text{eq}} = 5.8 \cdot \text{Nb} + 5 \cdot \text{Ti} \cdot \text{Si}$  is higher or equal to 4.5.

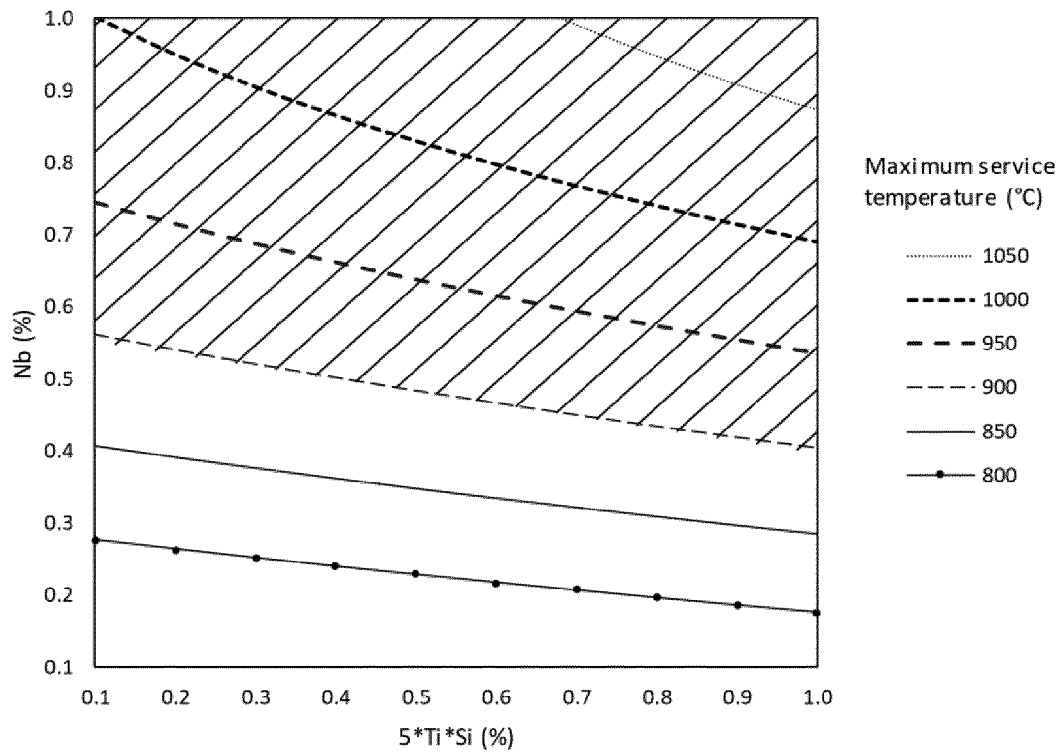


Fig. 1

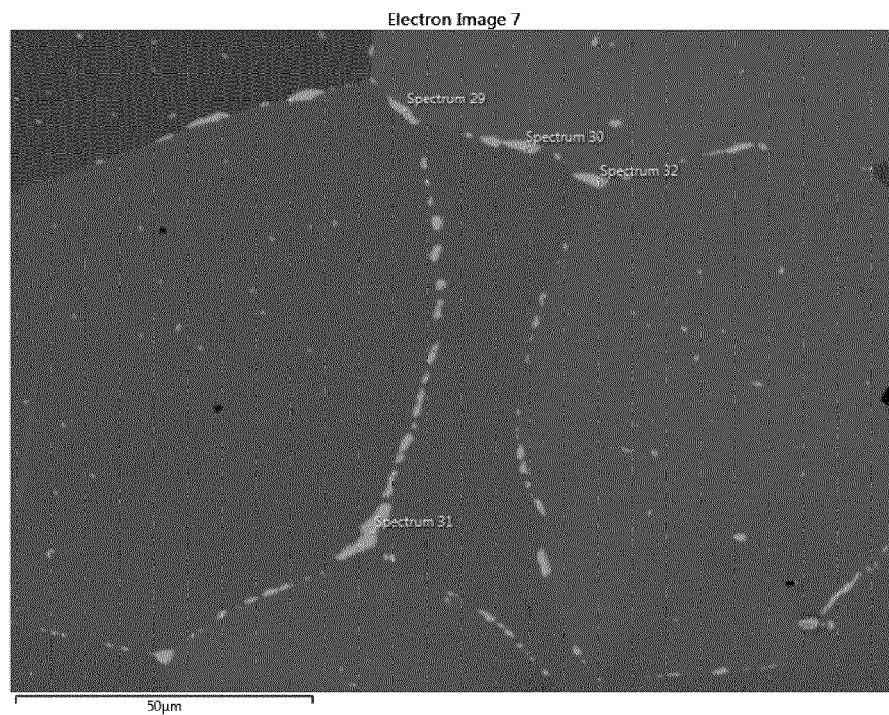
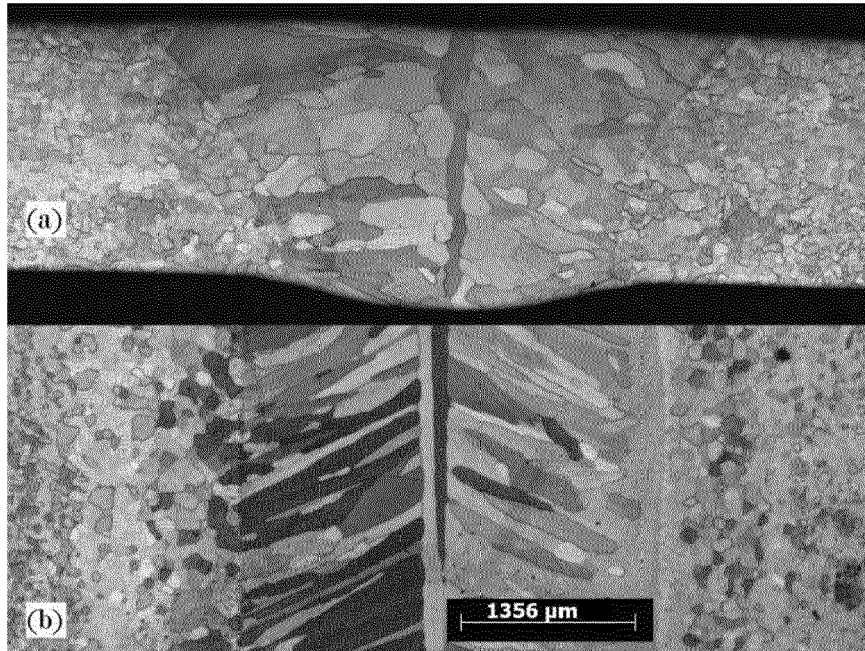
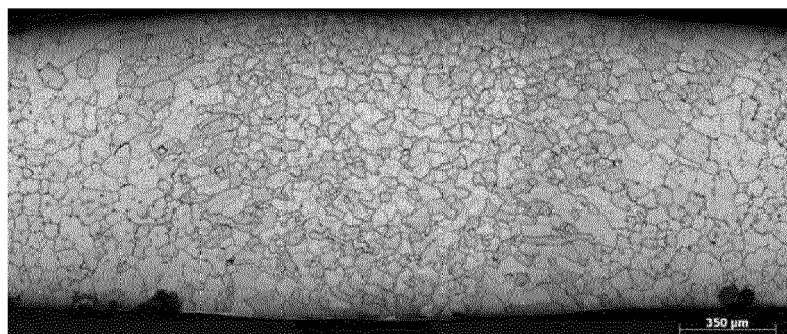


Fig. 2



**Fig. 3**



**Fig. 4**



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			C22C
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Place of search <b>The Hague</b>		Date of completion of the search <b>14 March 2019</b>	Examiner <b>Kreutzer, Ingo</b>
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