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(54) **FERRITIC STEEL FOR SERVICE TEMPERATURES FROM 650 TO 700 °C**

(57) A ferritic steel for service temperatures from 650 to 700 °C is described. In order to provide such a ferritic steel which can be used for thermomechanically high stressed components in thermal power plants and overcomes the disadvantages of usually used martensitic and austenitic steels, it is suggested, that the steel composi-

tion comprises 0.04 to 0.06 wt % Carbon, 13 to 16 wt % Chromium, 1.5 to 2.5 wt % Nickel, 1.5 to 4 wt % Cobalt, 5 to 10 wt % Tungsten, 0.05 to 0.25 wt % Vanadium, 0.01 to 0.065 wt % Niobium, up to 0.01 wt % Nitrogen and 0.01 to 0.02 wt % Boron, and exhibits a martensitic phase with a phase fraction from 10 to 30 % in the solid state.

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Description

[0001] The invention relates to a ferritic steel for service temperatures from 650 to 700 °C.

[0002] In the context of thermal power plants certain machine parts usually must withstand long term service temperatures from 650 to 700 °C in a thermomechanically and chemically demanding environment. For this purpose, martensitic or austenitic steel compositions exhibiting a martensitic respectively an austenitic phase are used due to their relatively high toughness at raised temperatures. Martensitic steels exhibit a fully martensitic structure and just in some cases some small fractions of ferrite can be detected in the microstructure. Austenitic steels usually exhibit a fully austenitic microstructure. Commonly used steel grades used in thermal power plants are for example martensitic steels such as P91, P92, T/P2, T/P23, T/P24, NF12, P122 or VM12 and austenitic steels such as TP347HFG, 304H UNS S30432, HR3C/310NbN or Sanicro 25.

[0003] The above mentioned martensitic steels nevertheless exhibit lower creep strength and higher coefficients of thermal expansion and also suffer from relatively low corrosion resistance in comparison to ferritic steels, particularly ferritic steels with at least 13 wt % Chromium, whereas austenitic steels represent even higher coefficients of thermal expansion than martensitic steels. Thermal power plant components of such martensitic and austenitic steels with higher coefficients of thermal expansion generate higher internal tension during frequent start ups and shutdowns, which ultimately lead to thermomechanical fatigue damages in thick components of thermal power plants. In Addition, austenitic steels also are relatively cost expensive.

[0004] However, although ferritic steels with at least 13 wt % Chromium exhibit an improved corrosion resistance, higher creep strength as well as lower coefficients of thermal expansion when compared to the above mentioned martensitic and austenitic steels, such ferritic steels have a relatively high ductile-brittle transition temperature (DBTT) which leads to a lower toughness at room temperature. As a consequence, such ferritic steels are not suited as a material for thermomechanically high stressed components in thermal power plants.

[0005] The invention is therefore based on the task of providing a ferritic steel for service temperatures from 650 to 700 °C, which steel can be used for thermomechanically high stressed components in thermal power plants and overcomes the disadvantages of usually used martensitic and austenitic steels.

[0006] The invention solves this problem in that the steel composition comprises 0.04 to 0.06 wt % Carbon, 13 to 16 wt % Chromium, 1.5 to 2.5 wt % Nickel, 1.5 to 4 wt % Cobalt, 5 to 10 wt % Tungsten, 0.05 to 0.25 wt % Vanadium, 0.01 to 0.065 wt % Niobium, up to 0.01 wt % Nitrogen and 0.01 to 0.02 wt % Boron, and exhibits a martensitic phase with a phase fraction from 10 to 30 % in the solid state. This means, that the steel exhibits a

ferritic structure containing a phase fraction of ferrite from 70 to 90 % and a phase fraction of martensite from 10 to 30 % in the solid state.

[0007] The invention is based on the realization, that the presence of Boron in combination with the lower concentration of Nitrogen of 0.01 wt % at the maximum has advantageous effects on the microstructure of ferritic steels. On the one hand, Nitrogen acts similar to Carbon in the context of steels, and increases the stability of the gamma structure, which consequently will increase the phase fraction of martensite during cooling processes. Small amounts of Nitrogen in ferritic steels are essential to improve the creep strength of the steel by the formation of MX (Nb, V) (C, N) carbon nitrides in the early stages of service. However, such carbon nitrides can transform to a Z-Phase in the presence of Chromium, Vanadium and / or Niobium after a while during service conditions at high temperature under high tension. This leads ultimately to a lowering in creep strength. On the other hand, Boron can diffuse in the presence of Chromium to M₂₃C₆ carbides and form the phase M₂₃(B,C)₆, which eventually decreases the growth rate of the carbides, especially at high temperatures. Consequently, the carbides remain small at grain- and sub-grain-boundaries. The presence of smaller carbides with higher number densities at grain boundaries can control or limit the growth of grain or sub-grain boundaries during operation. Since Boron is a relatively small element, it can be bound by vacancies in the steel matrix to reduce the self-diffusion of the steel matrix. In addition, Boron can generate a Cottrell atmosphere around dislocations and decreases the gliding rate of dislocations. Consequently, the creep strength of the ferritic steel is improved. Nevertheless, a high concentration of Boron in the steel besides higher concentrations of Nitrogen leads to the formation of the coarse Boron-Nitrogen phase, which can lead to an embrittlement of the steel matrix together with the creep strength reducing effect due to the formation of the Z-phase formation from carbon nitrides. In addition, it is believed that the addition of Nitrogen can reduce the impact toughness of the steel. Therefore, the simultaneous presence of Boron and Nitrogen in steels would normally lead to lower toughness and a relatively higher DBTT.

[0008] To overcome this disadvantage, it has surprisingly been shown according to the invention, that the above mentioned steel composition 0.009 to 0.02 wt % Boron and of up to 0.01 wt % Nitrogen together with the other elements creates the prerequisite, that the ferritic steel exhibits a martensitic phase fraction from 10 to 30 %, preferably from 10 to 23 % and even more preferably a martensitic phase fraction from 12 to 17 % in the solid state, depending on the cooling rate. The remaining phase fraction is always a ferritic phase. A ferritic steel with a martensitic phase fraction from 10 to 30 % leads to a lower residual stress in the material as well as to an improvement in absorbable impact energy and thus significantly reduces the DBTT without compromising a sufficient creep strength and corrosion resistance compared

to other ferritic steels with a Chromium content of over 13 wt %. If the ferritic steel exhibits a martensitic phase fraction from 10 to 23 %, particularly from 12 to 17 %, even a further lowering in residual stress as well as more improvement in absorbable impact energy can be achieved, which reduces the DBTT further. Although the formation of a martensitic phase would normally lead to a rise in the coefficient of thermal expansion of the ferritic steel, the martensitic phase fraction from 10 to 30 % enables a linear coefficient of thermal expansion which is for example about 11 % lower in comparison to a martensitic P91 steel and about 31 % lower in comparison to an austenitic Sanicro 25 steel. As a result, the ferritic steel according to the invention is ideally suited as a material for components of thermal power plants at service temperatures from 650 to 700 °C.

[0009] For even better creep properties and an improved toughness, it is recommended that the steel composition according to the invention comprises 1.5 to 2.5 wt % Cobalt, 5 to 8 wt % Tungsten, 0.2 to 0.25 wt % Vanadium, 0.055 to 0.065 wt % Niobium and 0.009 to 0.015 wt % Boron.

[0010] To improve the overall performance of the ferritic steel at service temperatures from 650 to 700 °C, it is suggested, that the steel composition further comprises 0.5 to 1.5 wt % Molybdenum, up to 0.25 wt % Silicon and up to 0.55 wt % Manganese.

[0011] Preferably, the ferritic steel according to the invention contains, in addition to Iron, exclusively the alloy elements Carbon, Chromium, Nickel, Cobalt, Molybdenum, Tungsten, Vanadium, Niobium, Nitrogen, Boron, Silicon and Manganese.

Example:

[0012] A ferritic steel according to the invention comprises 0.041 wt % Carbon, 14.98 wt % Chromium, 1.99 wt % Nickel, 2.54 wt % Cobalt, 0.84 wt % Molybdenum, 5.97 wt % Tungsten, 0.22 wt % Vanadium, 0.055 wt % Niobium, 0.0093 wt % Nitrogen, 0.0094 wt % Boron, 0.19 wt % Silicon and 0.5 wt % Manganese.

[0013] Depending on the cooling rates of the cooling process that is conducted with the ferritic steel from 1200 °C to room temperature, a martensitic phase fraction of 29 % can be achieved, with a ferritic phase as the remaining phase fraction. For this purpose, the cooling rate has to be at least 5 K/s, measured at a temperature window between 717 - 550 °C. The cooling media is for example air, water or oil.

[0014] If the cooling is conducted for example as oil quenching with a cooling rate of about 15 K/s, measured at a temperature window between 717 - 550 °C, the achieved martensitic phase fraction in the ferritic steel will be about 20 - 23 %. The DBTT is around 60 °C. The linear coefficient of thermal expansion is in the region of $9 \cdot 10^{-6}$ to $14 \cdot 10^{-6}$ K⁻¹.

[0015] A martensitic phase fraction in the ferritic steel as low as 12 - 17 % can be achieved for instance, if the

cooling is conducted as water quenching with a cooling rate of about 50 K/s, measured at a temperature window between 717 - 550 °C.

Claims

1. Ferritic steel for service temperatures from 650 to 700 °C, wherein the steel composition comprises 0.04 to 0.06 wt % Carbon, 13 to 16 wt % Chromium, 1.5 to 2.5 wt % Nickel, 1.5 to 4 wt % Cobalt, 5 to 10 wt % Tungsten, 0.05 to 0.25 wt % Vanadium, 0.01 to 0.065 wt % Niobium, up to 0.01 wt % Nitrogen and 0.009 to 0.02 wt % Boron, and wherein the steel exhibits a martensitic phase with a phase fraction from 10 to 30 % in the solid state.
2. Ferritic steel according to claim 1, wherein the steel composition comprises 1.5 to 2.5 wt % Cobalt, 5 to 8 wt % Tungsten, 0.2 to 0.25 wt % Vanadium, 0.055 to 0.065 wt % Niobium and 0.009 to 0.015 wt % Boron.
3. Ferritic steel according to claim 1 or 2, wherein the steel composition further comprises 0.5 to 1.5 wt % Molybdenum, up to 0.25 wt % Silicon and up to 0.55 wt % Manganese.
4. Ferritic steel according to any one of claims 1 to 3, wherein the steel exhibits a martensitic phase with a phase fraction from 10 to 23 % in the solid state.
5. Ferritic steel according to any one of claims 1 to 4, wherein the steel exhibits a martensitic phase with a phase fraction from 12 to 17 % in the solid state.



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The present search report has been drawn up for all claims			
Place of search The Hague		Date of completion of the search 31 October 2021	Examiner Vlassi, Eleni
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**ANNEX TO THE EUROPEAN SEARCH REPORT
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5 This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
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