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(54) **Ferritic heat-resistant steel and method for producing it**

(57) The invention provides a ferritic heat-resistant steel having excellent high-temperature oxidation resistance, especially excellent steam oxidation-resistant characteristics. In high-Cr ferritic heat-resistant steel, ultra-fine oxide particles having a size of not larger than 1 μm are formed just below the oxide films and formed on the steel base, whereby the adhesiveness between the films and the base is enhanced.
The ferretic heat-resistant steel consists of:

C from 0.02 to 0.18%
Si up to 1.0%, Mn up to 1.5%, P up to 0.030%, S up to 0.015%
Cr from 8.0 to 13.0%
Mo up to 2%, W up to 4%, with W + 2Mo ≤4%
V from 0.10 to 0.50%, Nb from 0.02 to 0.14%
either Ti and/or Y, with $0.01 \leq$ Ti + Y $\leq 0.30\%$
either Rh and/or Ir, with $0.3\% \leq$ Rh + (1/2)Ir $\leq 5\%$
either Pd and/or Pt in a total amount between 0.3 and 5% balance Fe

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Description

FIELD OF THE INVENTION

[0001]   The present invention relates to ferritic heat-resistant steel and to a method for producing it. More precisely, it relates to ferritic heat-resistant steel suitable for materials for apparatus that are used under high-temperature and high-pressure conditions, such as boilers, apparatus in chemical industry, etc., and to a method for producing it. Specifically, it relates to ferritic heat-resistant steel having excellent oxidation-resistance at high temperatures, especially steam oxidation-resistance which are not worsened even at high temperatures higher than 630°C, and having high creep strength which is comparable to that of ordinary steel, and relates to a method for producing it.

BACKGROUND OF THE INVENTION

[0002]   In general, heat-resistant steel for use for high-temperature heat-resistant and pressure-resistant parts of boilers, atomic powered apparatus and other apparatus in chemical industry is required to have high-temparature strength, toughness, high-temperature erosion resistance, oxidation resistance, etc. For those, austenitic stainless steel such as JIS-SUS321H, JIS-SUS347H, etc.; low-alloy steel such as JIS-STBA24 (2·1/4Cr-1Mo steel), etc.; and 9 to 12 Cr-type, high-ferrite steel such as JIS-STBA26 (9Cr-1Mo steel) have heretofore been used.

[0003]   Above all, high-Cr ferritic steel is widely used in the art, as having various advantages. Specifically, it has higher strength and higher erosion resistance at temperatures falling between 500 and 650°C than low-alloy steel, and is more inexpensive than austenitic stainless steel. Further, as its thermal conductivity is high and its thermal expansion is small, high-Cr ferrite steel has good thermal fatigue-resistance while hardly causing scale peeling and stress erosion cracking.

[0004]   On the other hand, in the recent thermal electric power plants, boilers are being driven under higher temperature and higher pressure conditions for the purpose of improving the thermal efficiency therein. At present, boilers in those plants are driven under a supercritical pressure condition at 538°C and 246 atmospheres, but will be driven under an ultra-supercritical pressure condition at 650°C and 350 atmospheres in future. Given that situation, steel for boilers is being required to have extremely high performance, and conventional high-Cr ferrite steel could no more satisfy the requirements of high oxidation resistance and long-term creep strength, especially steam oxidation-resistance. If the steam oxidation-resistance of boilers are poor, oxide films will be formed on the inner surfaces of steel pipes of boilers through which high-temperature steam passes. After having grown to a certain thickness, the oxide films peel off due to thermal stress that may be caused by the temperature change in boilers, for example, when boilers being driven are stopped, by which pipes will be clogged. Therefore, the prevention of steam oxidation of steel pipes, especially the prevention of peeling of oxide films is an important theme.

[0005]   As one material capable of satisfying the requirements noted above, known is austenitic stainless steel. However, austenitic stainless steel is expensive, and its use in commercial plants is limited because of the economic reasons. In addition, because austenitic stainless steel has a large thermal expansion coefficient, its thermal stress to be caused by the temperature change in drive stopping or the like is large. For these reasons, the use of austenitic stainless steel in plants is problematic because of the difficulties in designing and driving the plants using it. In view of these, it is desired to improve the performance of ferritic steel which has a smaller thermal expansion coefficient and is more inexpensive.

[0006]   In order to meet the requirements, recently, various types of ferritic heat-resistant steel have been proposed. For example, in Japanese Patent Application Laid-Open (JP-A) Hei-3-097832, Cu-containing, high-cr heat-resistant steel has been proposed, of which the W content is higher than that of conventional steel. Cu is added to this for improving its high-temperature oxidation resistance. In JP-A Hei-4-371551 and Hei-4-371552, high-Cr heat-resistant steel has been proposed. In this, the ratio of Mo/W is optimized, and Co and B are both added (thereto to) thereby increase the high-temperature strength and toughness of the steel. Even though their high-temperature creep strength is increased as a large amount of W is added thereto, those types of steel are still problematic in that the decrease in their toughness is inevitable. This is because W is a ferrite-forming element, like Mo and Cr, and therefore forma d-ferrite when added in such a large amount, whereby the toughness of the steel containing W is lowered.

[0007]   To solve this problem, it is most effective to form a martensitic single phase in steel. For this, for example, reducing the amount of Cr to be added to steel has been proposed in JP-A Hei-5-263195, etc.; and adding a large amount of austenite-forming elements such as Ni, Cu, Co and the like to steel has been proposed in JP-A Hei-5-311342, Hei-5-311343, Hei-5-311344, Hei-5-3111345, Hei-5-311-346, etc. These are to improve the toughness of steel by the proposed techniques.

[0008]   However, the former steel proposed in JP-A Hei-5-263196 could not have a sound scale structure since Mo enters the scale consisting essentially of Cr. Therefore, this has poor steam oxidation resistance. To solve this problem, another proposal has been proposed in JP-A Hei-8-85847, in which no Mo or only a small amount of Mo is added to

W-containing steel. In the steel proposed, W is an essential element added thereto for reinforcing it. However, as containing a large amount of Ni and Cu, this steel is still defective, like the steel disclosed in JP-A Hei-5-311342, in that it changes the structure of oxides consisting essentially of Cr_2O_3 and that its steam oxidation resistance is poor.

[0009] On the other hand, the high-Cr ferrite steel disclosed in JP-A-5-311342 and others has a low A_1 transformation point and a low A_3 transformation point, as containing a large amount of Ni, Cu, etc. As a result, the temper softening resistance of the steel is poor, and, in addition, carbides and nitrides in the steel rapidly aggregate to give large coarse grains therein. Therefore, the long-term creep strength of the steel is low. Moreover, Ni, Cu and other elements added to the steel change the scale layer formed to make it have a brittle structure, like in the heat-resistant steel disclosed in JP-A Hei-5-263196, whereby the steam oxidation resistance of the steel is worsened.

[0010] As mentioned hereinabove, known is no satisfactory ferritic heat-resistant steel having sufficient oxidation resistance and steam oxidation resistance for use in ultra-supercritical pressure conditions at high temperatures and high pressures.

SUMMARY OF THE INVENTION

[0011] The present invention has been made in consideration of the current situation noted above, and its subject matter is to provide ferritic steel which is free from the drawbacks of conventional ferritic steel. Specifically, the object of the invention is to provide ferritic steel, of which the steam oxidation resistance is not lowered even at high temperatures higher than 630°C, and which has excellent long-term creep strength.

[0012] In order to solve the problems noted above, the invention provides, as in claim 1, ferritic heat-resistant steel capable of forming an oxide film on its surface during use and having good steam oxidation-resistance, which is characterized in that ultra-fine oxide particles having a diameter of not larger than l micron are formed in and/or around the interface between the steel base and the oxide film formed thereon, to thereby increase the adhesiveness between the oxide film and the steel base.

[0013] The invention further provided the following:

Ferritic heat-resistant steel of claim 1, which contains from 8.0 to 13.0 % by weight of Cr and contains at least one of Ti and Y added thereto in a total amount of from 0.01 to 0.30 % by weight, as in claim 2;

Ferritic heat-resistant steel of claim 1 or 2, which has a composition comprising from 8.0 to 13.0 % (by weight - the same shall apply herein) of Cr; at least one of from 0.02 to 0.18 % of C, from 0.1 to 1.0 % of Si, from 0.05 to 1.5 % of Mn, from 0 to 0.5 % of Ni, from 0 to 4.0 % of W, from 0 to 2.0 % of Mo, provided that W + 2Mo ≤ 4 %, from 0.10 to 0.50 % of V, from 0.02 to 0.14 % of Nb, from 0 to 0.1 % of N, from 0 to 0.010 % of B and not larger than 0.010 % of O; at least one of Ti and Y in an amount of 0.01 % ≤ Ti + Y ≤ 0 30 %; and a balance of Fe and inevitable impurities, as in claim 3;

Ferritic heat-resistant steel of claim 3, which contains at least one of Co, Rh, Ir, Pd and Pt in a total amount of not larger than 5.0 % by weight, as in claim 4;

Ferritic heat-resistant steel having good steam oxidation-resistance and high long-term creep strength, which contains in an amount of from 8.0 to 13.0 % by weight and at least one of Rh and Ir in a total amount of from 0.3 to 5.0 % by weight, as in claim 5;

Ferritic heat-resistant steel of claim 5, which contains at least one of Rh and Ir in an amount of from 0.3 to 5.0 % (by weight - the same shall apply herein) of Rh and from 0.6 to 5.0 % of Ir and in a ratio of 0.3 % ≤ Rh + (1/2) Ir ≤ 5.0 %, as in claim 6;

Ferritic heat-resistant steel of claim 5 or 6, of which the lath structure is made fine and the martensite phase is reinforced by at least one of Rh and Ir added thereto, as in claim 7;

Ferritic heat-resistant steel of any one of claims 5 to 7, which Comprises from 0.06 to 0.18 % (by weight - the same shall apply herein) of C, from 0 to 1.0 % of Si, from 0 to 1.5 % of Mn, not larger than 0.030 % of P, not larger than 0.015 % of S, from 8.0 to 13.0 % of Cr, from 0 to 4.0 % of W, from 0 to 2.0 % of Mo, provided that W + 2Mo ≤ 4.0 %, from 0.030 to 0.14 % of Nb, from 0.10 to 0.50 % of V, from 0 to 0.10 % of N, from 0 to 0.030 % of B, not larger than 0.010 % of O, and from 0 to 0.050 % of sol. Al; at least one of Rh and Ir in a total amount of from 0.3 to 5.0 %; and a balance of Fe and inevitable impurities, as in claim 8;

Ferritic heat-resistant steel having steam oxidation resistance, which contains Cr in an amount of from 8.0 to 13.0 % by weight, and at least one of Pd and Pt in a total amount of from 0.3 to 5.0 % by weight, as in claim 9;

Ferritic heat-resistant steel of claim 9, which contains at least one of Pd and Pt in an amount of from 0.3 to 5.0 % (by weight - the same shall apply herein) of Pd and from 0.3 to 5.0 % of Pt and in a ratio of 0.3 % ≤ Pd + Pt ≤ 5.0 %, as in claim 10;

Ferritic heat-resistant steel of any of claim 9 or 10, which comprises from 0.06 to 0.18 % (by weight - the same shall apply herein) of C, from 0 to 1.0 % of Si, from 0 to 1.5 % of Mn, not larger than 0.030 % of P, not larger than 0.015 % of S, from 8.0 to 13.0 % of Cr, from 0 to 4.0 % of W, from 0 to 2.0 % of Mo, provided that W + 2Mo ≤ 4.0

%, from 0.030 to 0.14 % of Nb, from 0.10 to 0.50 % of V, from 0 to 0.10 % of N, from 0 to 0.030 % of B, not larger than 0.010 % of O, and from 0 to 0.050 % of sol. Al; at least one of Pd and Pt in a total amount of from 0.3 to 5.0 %; and a balance of Fe and inevitable impurities, as in claim 11; and

[0014]   A method for producing ferritic heat-resistant steel of any one of claims 1 to 4, which comprises heating steel at a temperature not lower than 1250°C, subjecting it to plastic working, such as forging, rolling or the like, then immediately keeping it at a temperature falling between 1000 and 1150°C for 1 hour or longer, and thereafter rapidly cooling it to a tewperature not higher than its martensitic transformation-finishing point thereby making it have a martensitic structure, and then heating and tempering it at a temperature falling between 650 and 800°C, as in claim 12.

BRIEF DESCRIPTION OF THE DRAWINGS

[0015]   Fig. 1 is a cross-sectional view of a steel sample of the invention, which graphically shows the relational structure of the oxide grains formed therein and the scale formed on the steel base.

[0016]   Fig. 2(A) is a cross-sectional view of a conventional steel sample in which the scale formed is peeling due to the voids formed therein; and Fig. 2 (B) is a cross-sectional view of a steel sample of the invention in which the scale formed is prevented from peeling due to the oxide particles formed therein.

[0017]   In those, 1 is an outer scale layer, 2 is an inner scale layer, 3 is a steel base, 4 is an oxide particle, and 5 is a void.

DESCRIPTION OF PREFERRED EMBODIMENTS

[0018]   The present invention is characterized by the features mentioned hereinabove. The problems with steel having poor oxidation resistance are that the oxide film formed on the inner surfaces of steel pipes peels off and deposits in the pipes to clog them, and that the peeled oxide film scatters in steel pipes and erodes the apparatus disposed in the later zone. From this viewpoint, the present invention has been made, and its subject matter is, as so mentioned hereinabove, to homogeneously form ultra-fine oxide particles having a size of not larger than 1 μm in and/or around the interface between the oxide film formed on the surface of a steel base and the steel base just below the oxide film, thereby improving the adhesiveness between the oxide film and the steel base.

[0019]   It is known that, in order to improve the high-temperature oxidation-resistance of steel, addition of a large amount of Cr or Si to steel to thereby make the steel have a high Cr or Si content is effective, However, high-Cr steel is problematic in that d-ferrite is formed therein to lower the toughness of the steel. Therefore, an austenite-stabilizing element such as Ni, Co, Cu or the like is added to conventional high-Cr steel. However, adding the element is disadvantageous, since a stable oxide film is difficult to form on the steel containing the element, resulting in that the oxidation resistance of the steel is reduced. On the other hand, high-Si steel is also defective in that the film formed thereon peels easily, even though its erosion is retarded.

[0020]   Given that situation, we, the present inventors have studied the structure of oxide films formed on various steel samples and also the structure of the film/steel interface in those samples, and those of film/steel interfacial structures, and have obtained the following findings. Based on those findings, we have completed the present invention.

(1) Fine oxide particles, if existing in/and or around the interface between a metal base and an oxide film formed thereon, especially in the region just below the film, could be void-filling points in the film and, in addition, could act as a barrier to the growth of voids being formed in the interface. Moreover, the adhesiveness between the film and the base is increased by the bridging effect of the particles, whereby the film is prevented from peeling.

(2) For forming such fine oxide particles, it is effective to add to steel an element having high affinity for oxygen, such as Ti or Y, in an amount of from 0.01 to 0.50 %. In addition, the element Ti or Y could trap oxygen, whereby the diffusion of oxygen into the inside of steel is prevented, and the oxidation speed in steel is much lowered.

(3) If too large oxide particles are formed in the region just below the film, however, they could no more resist the film peeling. Therefore, there is no significant difference between the presence of such large oxide particles and the absence of them

(4) In general, adding Ti to ordinary high-Cr ferritic heat-resistant steel produces coarse and large carbides, nitrides and carbonitrides particles (inclusions) in the steel, whereby the amount of carbides, nitrides and carbonitrides of V and Nb that contributes to the strengthening of the steel is greatly reduced, resulting in that the creep strength of the steel is lowered. For these reasons, in general, Ti is not added to the steel of that type. However, if the hot working conditions for the steel could be optimized, the carbides, nitrides and carbonitrides precipitated in the steel could be dispersed finely and the creep strength of the steel could be increased.

[0021]   Based on these results, the invention provides ferritic heat-resistant steel having both good oxidation resistance and high creep strength even at high temperatures of 600°C or higher.

[0022]   The constitution of the invention is described in more detail hereinunder.

<Oxide Precipitates>

[0023]   The essential reason for oxide film peeling is thermal stress to be caused by the temperature change in steel. The thermal stress shall be greater with the growth of the oxide film on steel (that is, with the increase in the thickness of the film). When the thermal stress exceeds the adhesiveness (adhesion strength) between the film and the underlying steel base, the film peels from the steel base. Therefore, increasing the adhesiveness of the film to the steel base is effective for preventing the film peeling.

[0024]   The film adhesiveness is generally increased by densifying the oxide film itself to produce the condition in which pores or voids are difficult to form in the interface between the film and the steel base. As opposed to this, however, in the present invention, fine particles are formed in the interface between the oxide film and the steel bade, so that they act as a barrier to the film peeling propagation in the film/base interface while preventing the film from swelling up.

[0025]   The scale peeling-preventing effect of the invention could be interpreted as follows:

[0026]   In the invention, for example, Ti or Y oxides are formed through internal oxidation in steel, while the steel is to have a scale structure composed of an outer scale layer (of Fe oxides) (1) and an inner scale layer (of Fe-Cr oxides) (2) as formed on the surface of the steel base (3), as in Fig. 1, in which fine oxide particles (4) exist around the scale/ base interface.

[0027]   In ordinary steel, it is believed that the pores existing in the scale will aggregate in the interface between the scale and the steel base to give voids (5), as in Fig. 2(A), and those voids (5) will be linked to each other to cause the scale peeling. However, as in Fig. 2(B), if fine oxide particles (4) exist around the interface between the scale layers (1) (2) and the steel base (3), especially in the region just below the scale (2), they could be void-filling points and even could act as a barrier to the linking of the voids (5). In addition, the particles could further act to mechanically bond the scale and the steel base, whereby the scale is prevented from being swelling up or peeling away.

[0028]   Existing oxide particles having a size of not larger than 1 micron, but preferably not larger than 0.5 microns in and/or around the interface between the oxide film and the steel base prevents the film from peeling, and is effective to attain the intended purpose. However, large particles having a size of 3 microns or larger, if existing in the interface, are not effective for the intended purpose, but rather promote the film peeling.

<Steel Composition>

[0029]

(1) Cr: In general, the oxide film formed on ferritic heat-resistant steel is composed of an outer layer consisting essentially of Fe oxides and an inner layer consisting essentially of Cr oxides or Fe-Cr oxides. Stabilizing the sound Cr_2O_3 film without peeling it is effective for improving the oxidation resistance of the steel. From this viewpoint, Cr is one essential alloying element in the invention. Regarding its amount to be added, Cr must be added to steel in an amount of not smaller than 8.0 % in order to form a sound oxide film. However, if the amount of Cr added is larger than 13.0 %, much Cr will promote the formation of d-ferrite, whereby the properties of the steel, including the toughness thereof, are much worsened. For these reasons, the Cr content of the steel of the invention preferably falls between 8.0 and 13.0 %.

(2) Ti: Ti has high affinity for oxygen. When added to steel in a small amount, Ti forms fine oxide particles just below the oxide film formed on steel. Ti easily bonds to not only oxygen but also carbon and nitrogen. Therefore, Ti added in steel alloys well bonds to those elements to form its carbides, etc. If the amount of Ti added is smaller than 0.01 %, all Ti will bond to carbon and other elements existing in steel alloys, and could no more form its oxides while the alloys are used. Therefore, it is desirable to add Ti to steel in an amount not smaller than 0.01 %. On the other hand, however, if the amount of Ti added is too large, Ti oxides formed will be in the form of coarse and large particles, and have some negative influences on steel. For these reasons, the uppermost limit of the amount of Ti to be added may be 0.3 %.

In addition, Ti traps oxygen. Therefore, adding Ti to steel prevents oxygen from diffusing into the inside of steel, whereby the oxidation speed in steel is greatly reduced.

On the other hand, Ti added to steel forms coarse and large carbides, nitrides and carbonitrides particles (inclusions) in the steel, whereby the amount of carbides, nitrides and carbonitrides of V and Nb that contributes to strengthen of the steel is greatly reduced, resulting in that the creep strength of the steel is lowered. For these reasons, in general, Ti is not added to ferritic heat-resistance steel. However, when Ti-adding steel is heated at temperatures of 1250°C or higher, the Ti carbides formed therein will be re-dissolved to form solid solution. Therefore, if Ti-added steel is subjected to predetermined plastic working, such as forging, rolling, extrusion or the like,

at temperatures falling within that range, and then immediately cooled to and kept at temperatures falling between 1000 and 1150°C, and thereafter further cooled to temperatures not higher than its martensitic transformation-finishing point, it may have a martensitic structure with no large and coarse Ti carbides. After this, the steel is tempered at temperatures falling between 650 and 800°C, whereby fine M23C6 and MC particles are precipitated in the tempered martensite phase. The creep strength of the thus-worked, Ti-added steel may be the same as that of the non-worked, Ti-free basic steel. The hot working is to promote the dissolution of Ti carbides in the steel, and therefore the hot working temperature is preferably higher. At 1250°C, the Ti carbides in the steel could be dissolved to form solid solution. Preferably, however, the steel is heated at temperatures not lower than 1300°C.

(3) Y: Like Ti, Y in an element having high affinity for oxygen, and this is effective for positively exhibiting the effect of the invention. Regarding its amount to be added, it is necessary that, like Ti, Y is added to steel in an amount larger than that capable of bonding to oxygen having dissolved in steel in order that Y added could bond with further oxygen in actual use of the steel. Therefore, the lowermost limit of the amount of Y to be added is 0.01 %, while the uppermost limit thereof may be 0.3 % for the same reasons as those for Ti. Also like Ti, Y traps oxygen. Therefore, adding Ti to steel prevents oxygen from diffusing into the inside of steel, whereby the oxidation speed in steel is greatly reduced.

Regarding those Ti and Y, where the two are both added to steel, the total amount of the two is suitably from 0.01 to 0.3%. If smaller than 0.01 %, they could not sufficiently exhibit the intended effect of the invention. However, if larger than 0.3 %, they will form coarse and large particles. Anyhow, the amount overstepping the range is unfavorable.

The other elements are added to steel, as in the prior art, for the purpose of making the steel have the necessary performance such as creep strength and toughness. For their amount, therefore, referred to is the ordinary knowledge known in the art.

(4) C: C is an element that forms carbides of various types, MC [as the case may be, in the form of carbonitrides, M(C,N), in which M indicates an alloying element, and the same shall apply hereunder], M_7C_3, M_6C and $M_{23}C_6$, and this has great influences on the properties of steel. In particular, fine carbide particles of VC, NbC and the like are precipitated in steel while the steel is used, and they contribute to the increase in the long-term creep strength of steel. In order that such fine carbide particles are effectively precipitated to strengthen steel, the amount of C to be in steel must not be smaller than 0.06 %. However, if larger than 0.18 %, too much C will form coarse and large aggregates of carbides in early stages in use, thereby undesirably lowering the long-term creep strength of steel. For these reasons, suitably, the C content of steel is defined to fall between 0.06 and 0.18 %.

(5) Si: Si is an element effective for deoxidizing steel melt and for improving the high-temperature steam oxidation resistance of steel. However, too much Si lowers the toughness of steel. Therefore, in general, the Si content of steel is defined to fall between 0.01 and 1.0 % in the prior art. Accordingly, also in the invention, the uppermost limit of the Si content is 1.0 %.

(6) Mn: Mn is an element to be added to steel for the purpose of deoxidizing and desulfurizing steel melt, and this is effective for increasing the short-term creep strength of steel under high stress. In order to attain its effect, Mn must be added in an amount not smaller than 0.05 %. On the other hand, however, if larger than 1.6 %, it is known that too much Mn lowers the toughness of steel. For these reasons, it is suitable that the amount of Mn to be added falls between 0.05 and 1.5 %.

(7) Mo, W: Mo is effective for solution strengthening of steel. In addition, it stabilizes $M_{23}C_6$ and increases the high-temperature strength of steel. However, if its amount is larger than 2 %, Mo promotes the formation of d-ferrite, while promoting the precipitation and aggregation of M_6C and Laves phases to give coarse and large particles. Therefore, its uppermost limit is defined to be 2 %. Like Mo, W is also suitable for solution strengthening of steel. In addition, this contributes the precipitation of fine particles of $M_{23}C_6$, while preventing carbides from being aggregated to give coarse and large particles. Owing to those effects, W greatly increases the high-temperature and long-term creep strength of steel. However, if larger than 4 %, too much W often forms d-ferrite and coarse Laves phases thereby lowering the toughness of steel. Therefore, it is suitable that the uppermost limit of W is 4 %. Where Mo and W are both added to steel, it is suitable that the total amount of W + 2Mo is up to 4 %.

(8) V: V is an element that forms fine carbides, nitrides and cabonitrides particles to contributes to the increase in the creep strength of steel. In order to attain its effect, V must be added to steel in an amount not smaller than 0.10 %. However, even if added in an amount larger than 0.50 %, too much V is no more effective, since the effect of V is saturated when its amount is up to 0.50 %. Therefore, it is suitable that the V content falls between 0.10 and 0.50 %.

(9) Nb: Nb precipitates in steel in the form of its carbides, nitrides and carbonitrides to thereby increase the high-temperature strength of steel. In addition, it acts to make the microstructure of steel fine, thereby increasing the toughness of steel. Therefore, it is said that the lowermost limit of Nb to be in steel is 0.02 %. However, it is believed that, if Nb is added in an amount of 0.15 % or more, it could not completely penetrate into the matrix of steel to form solid solution at normalizing temperatures, and therefore could not sufficiently exhibit its effect to strengthen

steel. Accordingly, it is suitable that the Nb content falls between 0.02 and 0.4 %.

(10) N: N is an element to form nitrides and carbonitrides to thereby increase the creep strength of steel. In general, however, if the N content is larger than 0.1 %, the nitrides formed grow much to give coarse and large particles, which rather greatly lower the toughness of steel. Therefore, the uppermost limit of the N content is preferably 0.1 %.

(11) Ni; Ni is an austenite-stabilizing element. It is known that this is effective for retarding the formation of d-ferrite and increasing the toughness of steel. However, if added in an amount larger than 1 %, too much Ni lowers the creep strength of steel. Therefore, the uppermost limit of Ni is preferably 1 %.

(12) B: It is known that B is effective for strengthening the intergranular strength of steel and for finely dispersing $M_{23}C_6$ carbides in steel, and that this contributes to the increase in the high-temperature strength of steel and is effective for improving the quenchability of steel. It is also known that too much B larger than 0.01 % forms coarse and large B-containing precipitates thereby embrittling steel. Therefore, it is suitable that the uppermost limit of B is 0.01 %.

(13) Co, Rh, Ir: Apart from those mentioned hereinabove, Co is known as an element effective for retarding the formation of δ-ferrite. The recent studies in the prior art are toward the addition of Co to steel. However, it is known that too much Co lowers the strength of steel and even embrittle steel. In general, it is said that the uppermost limit of Co is 5 %. Like Co, Rh and Ir are both effective. Co, Rh and Ir may be added to steel in an amount of from 0.3 to 5.0 % each. Where two or more of these are added, the total amount is suitably from 0.3 to 5.0 %

(14) Sol. Al: Al added to steel essentially acts as a deoxidizer for steel melt. In steel, Al added exists in the form of its oxides and in any other form. In analysis, the latter is referred to as HCl-soluble Al (sol. Al). So far as steel could be deoxidized by any other elements added thereto, sol. Al is not specifically needed. If added in an amount larger than 0.050 % by weight, too much Al will lower the creep strength of steel. The sol. Al content of steel is suitably from 0 to 0.050 % by weight.

(15) P and S: P and S are both inevitable impurities in steel. These elements have some negative influences on the hot workability of steel, the toughness of welded parts of steel, etc. Therefore, their content is preferably as small as possible. Specifically, P shall not be larger than 0.030 % by weight, and S not larger than 0.05 % by weight.

(16) O: O is also an inevitable impurity in steel. If it locally exist in steel in the form of coarse and large oxide particles, the particles have some negative influences on the toughness and other properties of steel. In order to ensure the toughness of steel, it is desirable that the O content of steel is minimized as much as possible. When the O content of not larger than 0.010 % by weight, its influence on the toughness of steel is satisfactorily small. Therefore, the O content shall not be larger than 0.010 %.

[0030] As so mentioned hereinabove, the subject matter of the present invention is to form fine oxide particles having a size of not larger than 1 micron just below the film formed on steel, whereby the film is prevented from pooling off owing to the bridging effect of the oxide particles. Needless-to-say, therefore, the components constituting the steel of the invention are not whatsoever limited to those specifically referred to hereinabove, so far as the steel attains the object of the invention.

[0031] In addition, the ferritic heat-resistant steel of the invention, which is characterized by the matters specifically mentioned hereinabove, has been completed on the basis of the following findings that have resulted from the data of the detailed studies, which the present inventors have made relative to the relationship between the property of the steel including its high, long-term creep strength and steam oxidation resistance, and the chemical components constituting the steel and the metallic structure (microstructure) of the steel.

<Long-Term Creep Strength>

[0032] Rh and Ir and also Co are all in the same Group of the Periodic Table, and they are austenite-forming elements. It has heretofore been believed that, when existing in steel, they greatly lower the Al transformation point of steel thereby lowering the temper softening resistance of steel.

[0033] However, even if Rh and Ir are added to high-Cr ferritic steel containing Mo and W, the A_1 transformation point of the steel is not so much lowered. In addition, being different from Co, Rh and Ir added to the steel do not promote the aggregation and growth of carbides, nitrides and carbonitrides into coarse and large particles. Adding Rh and Ir to the steel makes the martensitic lath structure of the steel fine, while strengthening the martensite phase in the steel. This phenomenon is confirmed in ordinary heat treatment of the steel. There is found no significant difference in the degree of hardness between the high-Cr ferritic steel and conventional steel after they are quenched, but the temper softening resistance of the high-Cr ferritic steel is much higher than that of conventional steel. After having been normalized and tempered, the high-Cr ferritic steel shall have a martensitic texture that contains carbides, nitrides and carbonitrides precipitated therein. The martensitic structure in the steel tends to recover and soften with the lapse of time at high temperatures higher than 630°C, which could be prevented by Rh and Ir added to the steel.

[0034] As a result, the long-term creep strength of the steel at high temperatures higher than 630°C is greatly in-

creased, and the steel shall have excellent long-term creep strength. <Steam Oxidation Resistance>

[0035] Even if Rh and Ir are added to high-cr ferritic steel containing much Mo and W, they do not convert the sound, corundum-type scale layer consisting essentially of Cr_2O_3 and formed on the steel into a spinel-type structure. Therefore, the scale layer formed on the steel is not broken, and the steam oxidation resistance of the steel is not lowered even at high temperatures higher than 630°C.

[0036] The effect of Rh and Ir is noticeable when at least any one of the two is added to the steel in an amount of from 0.3 to 5 % by weight, but preferably when Rh is added thereto in an amount not smaller than 0.3 % by weight and/or Ir is added in an amount not smaller than 0.6 % by weight. However, too much Rh and Ir larger than 5 % by weight each, even if added to the steel, will saturate their effect without augmenting it any more. For these reasons, suitably, the amount of Rh and Ir to be added is from 0.3 to 5.0 % by weight and that of Ir is from 0.6 to 5.0 % by weight.

[0037] The effect of these elements noted above can be attained when Rh and Ir are both added to the steel. In the combined addition, however, the amount of the two shall be 0.3 % ≤ Rh + (1/2)Ir ≤ 5.0 %, in which % being by weight, in view of their ability to exhibit and saturate the effect.

[0038] The ferritic heat-resistant steel of the invention can be produced in any ordinary equipment and process generally employed in the prior art.

[0039] For example, steel is melted in a furnace such as an electric furnace, a converter or the like, and deoxidizers and alloying elements are added thereto to control the steel composition. When strict modulation of the steel composition is specifically needed, the steel melt may be subjected to vacuum treatment prior to adding alloying elements thereto.

[0040] The steel melt having been specifically modulated to have a predetermined chemical composition is then cast into slabs, billets or ingots in a continuous casting method or a slabmaking method, and which are thereafter shaped into pipes, sheets, etc. Where seamless steel pipes are produced, for example, billets are extruded or forged into them. For producing steel sheets, slabs are hot-rolled into hot-rolled sheets. The resulting hot-rolled sheets may be cold-rolled into cold-rolled sheets. Where the hot-working is followed by the cold-working such as cold-rolling, it is desirable that the hot-worked sheets are annealed and washed with acids prior to being subjected to ordinary cold-working.

[0041] The thus-produced steel pipes and sheets may be optionally subjected to heat treatment such as annealing or the like, to thereby make them have predetermined characteristics.

[0042] The invention is described in more detail hereinunder with reference to the following Examples, which, however, are not intended to restrict the scope of the invention.

Example 1

[0043] Various types of steel each having the chemical composition shown in Table 1 below were produced in a vacuum induction smelting furnace having a capacity for 50 kg steel. Ingots produced were hot-forged and hot-rolled into sheets having a thickness of 20 mm, from which test pieces were sampled. In Table 1, Comparative Samples 1, 2 and 3 are samples of standard steel of ASTM T91, T92 and T122, respectively.

Table 1 - Chemical Composition of Steel Samples (wt.%)

Type of steel	C	Si	Mn	Cr	Mo	W	V	Nb	N	Ni	Ti	Y	Others
Comparative Sample 1	0.12	0.45	0.42	8.9	0.99	-	0.21	0.06	0.05	0.08	-	-	-
Comparative Sample 2	0.12	0.02	0.47	9.1	0.48	1.81	0.21	0.05	0.04	0.06	-	-	B: 0.003
Comparative Sample 3	0.13	0.26	0.61	10.3	0.35	2.2	0.22	0.05	0.06	0.32	-	-	Cu: 0.50 B: 0.003
Comparative Sample 4	0.10	0.05	0.41	9.1	0.50	1.79	0.25	0.05	0.01	-	0.008		
Sample 1 of the Invention	0.11	0.06	0.45	9.0	0.51	1.81	0.23	0.05	0.01	-	0.03		
Sample 2 of the Invention	0.11	0.09	0.44	9.0	0.51	1.81	0.23	0.05	0.02	-	0.1		
Sample 3 of the Invention	0.12	0.07	0.46	9.1	0.48	1.77	0.24	0.05	0.01	-	0.25		
Comparative Sample 5	0.11	0.06	0.51	8.9	0.50	1.82	0.22	0.05	0.02	-	0.5		
Comparative Sample 6	0.10	0.10	0.40	9.0	0.51	1.80	0.23	0.05	0.01	-	-	0.006	
Sample 4 of the Invention	0.12	0.08	0.50	9.0	0.52	1.81	0.25	0.05	0.01	-	-	0.05	
Sample 4 of the Invention	0.10	0.07	0.45	9.0	0.51	1.78	0.22	0.05	0.01	-	-	0.1	
Sample 4 of the Invention	0.11	0.07	0.46	9.1	0.52	1.80	0.24	0.05	0.02	-	0.05	0.05	

[0044]   Prior to being subjected to steam oxidation tests for evaluating their steam oxidation resistance, all test pieces were pre-treated for AC normalization at 1050°C for hours followed by AC tempering at 780°C for 1 hour. In one steam oxidation test, each test piece was kept heated in a steam atmosphere at 700°C for 1000 hours, and the thickness of the scale layer formed was measured. In another heat-cycle test, each test piece was heated at the same temperature of 700°C for 96 hours, and then cooled to room temperature, and the heat cycle was repeated for a total of 10 times. After the heat-cycle test, the amount of scale peeled off was measured.

[0045]   The data obtained in those tests are shown in Table 2, in which are also shown the presence or absence of oxide particles just below the scale layer and the size of the oxide particles formed.

Table 2 - Data in Steam Oxidation Tests

Type of Steel	Thickness of Scale Formed in Continuous Heating (microns)	Amount of Scale Peeled off in Cycle Heating (mg)	Oxide Particles Formed Just Below Scale Layer	Maximum Diameter of Oxide Particles Formed Just Below Scale Layer (microns)
Comparative Sample 1	137	158	Yes	3.8 (in laminar distribution)
Comparative Sample 2	201	268	No	-
Comparative Sample 3	98	106	Yes	2.7 (in laminar distribution)
Comparative Sample 4	188	215	No	-
Sample 1 of the Invention	93	89	Yes	0.03
Sample 2 of the Invention	72	43	Yes	0.12
Sample 3 of the Invention	89	76	Yes	0.63
Comparative Sample 5	143	131	Yes	1.4
Comparative Sample 6	175	187	No	-
Sample 4 of the Invention	84	38	Yes	0.04
Sample 5 of the Invention	66	69	Yes	0.23
Sample 6 of the Invention	73	124	Yes	0.05

[0046]   As in Table 2, it has been confirmed that Ti and Y added to steel gave fine oxide particles in the region below the scale layer formed, by which the amount of the scale peeled off in the heat-cycle test was reduced. In addition, in the continuous heating test, the thickness of the scale layer formed on the steel samples containing any of Ti and Y added thereto was reduced, from which it is understood that the oxidation speed in those steel samples was retarded.

[0047]   Even in the comparative steel samples to which Si had been added, the thickness of the scale layer formed in the continuous heating test was reduced, and some oxide particles were formed just below the scale layer. However, in those Si-containing comparative samples, the oxide particles formed were relatively large and existed inside the Cr_2O_3 layer in laminar distribution. Therefore, in those, it is believed that the oxide particles formed rather promoted the peeling of the scale layer.

Example 2

[0048]   Sample 2 of the invention in Table 1 was forged at different temperatures falling between 1100 and 1400°C, then immediately inserted into a furnace at 1050°C and kept therein for 1 hour, and thereafter cooled with water. After this, the thus-processed samples were post-treated for AC tempering at 780°C for 1 hour. Then, these were subjected to a creep rupture test at 650°C and under 100 MPa. The data obtained are shown in Table 3.

Table 3 -

Change in Creep Rupture Strength, depending on hot-working temperature (normalization: 1050°C x 1 hr, tempering: 780°C x 1 hr)		
Type of Steel	Heating Temperature (°C)	Time before Rupture at 650°C and under 100 MPa (hrs)
Comparative Sample 1	1200	1013
Comparative Sample 2	1200	5931
Comparative Sample 3	1200	6248
Sample 2 of the Invention	1100	630
	1200	814
	1250	1103
	1300	5981
	1350	6436
	1400	7124

[0049]   As in Table 3, the time before creep rupture of Sample 2 of the invention, which had been hot-worked at temperatures of 1250°C or higher, was prolonged to be longer than that of Comparative Sample 1, T91. In addition, the creep rupture strength of Sample 2 of the invention, which had been hot-worked at 1400°C, was much increased to be nearly comparable to that of T92 (Comparative Sample 2) and T122 (Comparative Sample 3). The test data support the high creep strength of Sample 2 of the invention.

Example 3

[0050]   various types of steel each having the chemical composition shown in Table 4 below were produced in a vacuum high-frequency induction furnace having a capacity for 10 kg steel.

Table 4

Sample	C / P	Si / S	Mn / Cr	W / Rh	Mo / Ir	W + 2Mo + Rh + (1/2)Ir	Nb / B	V / O	N / So. Al	Others
Samples of the Invention										
1	0.09	0.15	0.53	3.23	0	3.23	0.04	0.18	0.052	
	0.001	0.001	9.25	0	3.77	1.885	0.005	0.005	0.003	
2	0.14	0.33	0.99	2.65	0.43	3.51	0.06	0.25	0.002	
	0.025	0.002	9.03	1.23	1.05	1.756	0.003	0.003	0.012	
3	0.08	0.78	-	2.83	0.22	3.27	0.06	0.22	0.062	
	0.003	38.01	11.8	3.16	0	3.16	-	0.008	0.028	
4	0.16	0.02	0.21	3.02	0.06	3.14	0.08	0.19	0.002	
	0.001	0.005	10.4	0	2.04	1.02	0.003	0.009	0.001	
5	0.13	0.54	0.55	1.56	0.75	3.06	0.03	0.28	0.018	
	0.014	0.002	8.85	2.11	0	2.11	0.004	0.001	-	
6	0.07	0.14	1.32	0	1.66	3.3	0.006	0.24	0.042	
	0.024	0.006	8.92	0.37	2.65	1.695	0.006	0.008	0.015	
Comparative Samples										
1	0.11	0.42	0.56	-	0.96	1.92	0.07	0.21	0.051	Ni 0.06
	0.014	0.006	8.67	-	-	-	-	N/A	0.012	
2	0.22	0.51	0.43	0.57	1.03	2.63	-	0.35	0.041	Ni 0.15
	0.011	0.006	12.12	-	-	-	-	N/A	0.021	

[0051]   Each steel melt was cast into ingots having a diameter of 70 mm, which were then hot-forged at a temperature varying from 1250°C to 1000°C into sheets having a square of 45 mm x 45 mm and a length of 400 mm. Then, these were cold-rolled at a temperature varying from 1100°C to 900°C into sheets having a square of 15 mm x 15 mm.

[0052]   Samples Nos. 1 to 6 of the invention in Table 4 were thereafter kept at 1100°C for 1 hour and then normalized by air cooling, or were kept at 800°C for 1 hour and then tempered by air cooling.

[0053]   On the other hand, Comparative Samples 1 and 2 in Table 4 were subjected ordinary post-heat-treatment. Briefly, these were kept at 950°C for 1 hour and then normalized by air cooling, or were kept at 750°C and then tempered by air cooling. Comparative Samples 1 and 2 had a chemical composition of ASTM-A213-T91 and DIN-X20CrMoWV121, respectively.

[0054]   Test pieces were sampled out of those eight samples, and tested for the high-temperature creep strength and the steam oxidation resistance.

(High-Temperature Creep Strength]

[0055]   The test pieces were subjected to a creep rupture test, for which the test condition is mentioned below.

Test Piece	diameter 8.0 mm gauge length 40 mm
Test Temperature	(1) 650°C, (2) 700°C
Stress	(1) 140 MPa, (2) 120 MPa
Measured Matter	Time before Rupture

[Steam Oxidation Resistance]

[0056]   The test pieces were subjected to a steam oxidation test, for which the test condition is mentioned below.

Test Atmosphere	steam atmosphere at 700°C
Test Time	1000 hours
Measured Matter	Thickness of scale formed

[0057]   The data obtained in those tests are shown in Table 5.

Table 5

		Time before Creep Rupture (hrs) 650°C, 140 MPa	Time before Creep Rupture (hrs) 700°C, 120 MPa	Mean Thickness of Scale Formed in Steam Oxidation (μm) 700°C x 1000 hrs
Samples of the Invention	1	3542	187	61
	2	3216	251	70
	3	3733	316	73
	4	4308	269	68
	5	3884	364	52
	6	4336	402	77
Comparative Samples	1	65	0.5	151
	2	52	1.3	66

[0058]   As in Table 5, the time for creep rupture of all Samples 1 to 6 of the invention at 650°C and under 140 MPa was longer than 3000 hours, and that at 700°C and under 120 MPa was longer than 100 hours. In those Samples 1 to 6 of the invention, the mean thickness of the scale layer formed in the steam oxidation test at 700°C for 1000 hours was not larger than 77 μm.

[0059]   On the other hand, the creep rupture strength of Comparative Samples 1 and 2 was much inferior to that of Samples 1 to 6 of the invention, as in Table 5. Regarding the steam oxidation resistance, the thickness of the scale layer formed in Comparative Sample 1 was about 2 times that in Samples 1 to 6 of the invention. This means that the

steam oxidation resistance of Comparative Sample 1 is poor.

[0060] From the test results mentioned above, it is confirmed the steam oxidation resistance of the ferritic heat-resistant steel of the invention is not lowered even at high temperatures higher than 630°C and that the steel has high creep strength.

Example 4

[0061] Various types of steel each having the chemical composition shown in Table 6 below were produced in a vacuum high-frequency induction furance having a capacity for 10 kg steel.

Table 6

		C	P	Si	S	Mn	Cr	W	Pd	Mo	Pt	W+2Mo	Pd+Pt	Nb	B	V	O	N	sol. Al	
Samples of the Invention	1	0.09	0.021	0.03	0.001	0.48	8.87	2.67	3.25	0.15	0	2.97	3.25	0.03	0.003	0.2	0.002	0.048	0.002	
	2	0.12	0.003	0.51	0.001	0.82	9.02	3.01	0	0.32	3.17	3.65	3.17	0.09	-	0.21	0.006	0.007	0.014	
	3	0.07	0.008	0.33	0.003	0.41	8.65	3.23	2.32	0	0.23	3.23	2.55	0.07	0.002	0.29	0.009	0.061	0.035	
	4	0.11	0.017	0.12	0.002	0.2	9.33	2.03	2.45	0.58	0.51	3.19	2.96	0.06	0.006	0.37	0.008	0.053	0	
	5	0.15	0.023	0.34	6E-04	-	10.8	0.65	1.22	1.33	0.38	3.31	1.60	0.07	0.003	0.19	0.003	0.002	0.001	
	6	0.09	0.002	0.39	0.001	0.83	9.49	0	0.56	1.53	2.35	3.06	2.91	0.06	0.008	0.25	0.007	0.047	0.032	
Comparative Samples	1	0.11	0.014	0.42	0.006	0.56	8.67	-	-	0.96	-	1.92	-	0.07	-	0.21	N/A	0.051	0.012	Ni 0.06
	2	0.22	0.011	0.51	0.006	0.43	12.12	0.57	-	1.03	-	2.63	-	-	-	0.35	N/A	0.041	0.021	Ni 0.15

[0062] Each steel melt was cast into ingots having a diameter of 70 mm, which were then hot-forged at a temperature varying from 1250°C to 1000°C into sheets having a square of 45 mm x 45 mm and a length of 400 mn. Then, these were cold-rolled at a temperature varying from 1100°C to 900°C into sheets having

a square of 15 mm x 15 mm.

[0063] Sampled Nos. 1 to 6 of the invention in Table 6 were thereafter kept at 1100°C for 1 hour and then normalized by air cooling, or were kept at 800°C for 1 hour and then tempered by air cooling.

[0064] On the other hand, Comparative Samples 1 and 2 in Table 6 were subjected ordinary post-heat-treatment. Briefly, these were kept at 950°C for 1 hour and then normalized by air cooling, or were kept at 750°C and then tempered by air cooling. Comparative Samples 1 and 2 had a chemical composition of ASTM-A213-T91 and DIN-X20CrMoWV121, respectively.

[0065] Test pieces were sampled out of those eight samples, and tested for the high-temperature creep strength and the steam oxidation resistance.

[Steam Oxidation-resistance]

[0066] The test condition is mentioned below.

Test Piece	diameter 8.0 mm
	gauge length 40 mm
Test Temperature	(1) 650°C, (2) 700°C
Stress	(1) 140 MPa, (2) 120 MPa
Measured Matter	Time before Rupture

[0067] The data obtained in those tests are shown in Table 7.

Table 7

		Time before Creep Rupture (h) 650°C, 140MPa	Time before Creep Rupture (h) 700°C, 120MPa	Average Thickness of Scale Formed in Steam Oxidation (μm) 625°C×1000h	Average Thickness of Scale Formed in Steam Oxidation (μm) 650°C×1000h	Average Thickness of Scale Formed in Steam Oxidation (μm) 700°C×1000h
Samples of the Invention	1	1211	121	22	31	43
	2	1765	106	23	37	45
	3	1553	129	31	35	38
	4	1638	113	36	42	51
	5	1247	170	29	38	44
	6	1450	155	32	48	57
Comparative Samples	1	65	0.5	82	136	151
	2	52	1.3	45	62	66

[0068] In case of samples 1 ~ 6, thickness of the scale layer formed, is less than 36μm (625 °C × 1000h), less than 48μm (650 °C × 1000h) and less than 57 μm (700 °C × 1000h). It was found that each steel of the samples 1 ~ 6 has superior steam oxidation-resistance at the high temperature of over 630°C and is extremely stable.

[0069]   Needless-to-say, the invention is not whatsoever limited by the embodiments illustrated hereinabove. For its details, the invention shall encompass any and every change and modification not overstepping its scope.

[0070]   As has been described in detail hereinabove, the present invention provides ferritic heat-resistant steel having excellent steam oxidation resistance and creep strength characteristics. The creep strength of the steel of the invention is at least comparable to or higher than that of conventional steel. The steel of the invention is useful for high-temperature heat-resistant and pressure resistant parts capable of being widely used in various industrial fields, for example, for those of boilers, atomic powered apparatus and other apparatus in chemical industry. For example, the steel may be used for pipes, sheets for pressure containers, turbines, etc.

Claims

1. Ferritic heat-resistant steel capable of forming an oxide film on its surface during use and having good steam oxidation-resistance, which is characterized in that ultra-fine oxide particles having a diameter of not larger than 1 micron are formed in and/or around the interface between the steel base and the oxide film formed thereon, to thereby increase the adhesiveness between the oxide film and the steel base.

2. Ferritic heat-resistant steel as claimed in claim 1, which contains from 8.0 to 13.0 % by weight of Cr and contains at least one of Ti and Y added thereto in a total amount of from 0.01 to 0.30 % by weight.

3. Ferritic heat-resistant steel as claimed in claim 1 or 2, which has a composition comprising from 8.0 to 13.0% (by weight - the same shall apply herein) of Cr; at least one of from 0.02 to 0.18 % of C, from 0.1 to 1.0 % of Si, from 0.05 to 1.5 % of Mn, from 0 to 0.5 % of Ni, from 0 to 4.0 % of W, from 0 to 2.0 % of Mo, provided that $W + 2Mo \leq$ 4 %, from 0.10 to 0.50 % of V, from 0.02 to 0.14 % of Nb, from 0 to 0.1 % of N, from 0 to 0.010 % of B and not larger than 0.010 % of O; at least one of Ti and Y in an amount of $0.01 \% \leq Ti + Y \leq 0.30 \%$; and a balance of Fe and inevitable impurities.

4. Ferritic heat-resistant steel having good steam oxidation-resistance and high long-term creep strengh, which contains at least one of Co, Rh, Ir, Pd and Pt in a total amount of not larger than 5.0 % by weight.

5. Ferritic heat-resistant steel as claimed in claim 1, which contains Cr in an amount of from 8.0 to 13.0 % by weight and at least one of Rh and Ir in a total amount of from 0.3 to 5.0 % by weight.

6. Ferritic heat-resistant steel as claimed in claim 5, which contains at least one of Rh and Ir in an amount of from 0.3 to 5.0 % (by weight - the same shall apply herein) of Rh and from 0.6 to 5.0 % of Ir and in a ratio of 0.3 % Rh + (1/2) Ir $\leq$ 5.0 %.

7. Ferritic heat-resistant stool as claimed in claim 5 or 6, of which the lath structure is made fine and the martensite phase is reinforced by at least one of Rh and Ir added thereto.

8. Ferritic heat-resistant steel as claimed in any one of claims 5 to 7, which comprises from 0.06 to 0.18 % (by weight - the same shall apply herein) of C, from 0 to 1.0 % of Si, from 0 to 1.5 % of Mn, not larger than 0.030 % of P, not larger than 0.015 % of S, from 8.0 to 13.0 % of Cr, from 0 to 4.0 % of W, from 0 to 2.0 % of Mo, provided that W + 2Mo $\leq$ 4.0 %, from 0.030 to 0.14 % of Nb, from 0.10 to 0.50 % of V, from 0 to 0.10 % of N, from 0 to 0.030 % of B, not larger than 0.010 % of O, and from 0 to 0.050 % of sol. Al; at least one of Rh and Ir in a total amount of from 0.3 to 5.0 %; and a balance of Fe and inevitable impurities.

9. Ferritic heat-resistant steel having steam oxidation resistance, which contains Cr in an amount of from 8.0 to 13.0 % by weight, and at least one of Pd and Pt in a total amount of from 0.3 to 5.0 % by weight.

10. Ferritic heat-resistant steel as claimed in claim 9, which contains at least one of Pd and Pt in an amount of from 0.3 to 5.0 % (by weight - the same shall apply herein) of Pd and from 0.3 to 5.0 % of Pt and in a ratio of 0.3 % $\leq$ Pd + Pt $\leq$ 5.0 %.

11. Ferritic heat-resistant steel as claimed in any of claim 9 or 10, which comprises from 0.06 to 0.18 % (by weight - the same shall apply herein) of C, from 0 to 1.0 % of Si, from 0 to 1.5 % of Mn, not larger than 0.030 % of P, not larger than 0.015 % of S, from 8.0 to 13.0 % of Cr, from 0 to 4.0 % of W, from 0 to 2.0 % of Mo, provided that W + 2Mo $\leq$ 4.0 %, from 0.030 to 0,14 % of Nb, from 0.10 to 0.50 % of V, from 0 to 0.10 % of N, from 0 to 0.030 % of

B, not larger than 0.010 % of O, and from 0 to 0.050 % of sol. Al; at least one of Pd and Pt in a total amount of from 0.3 to 5.0 %; and a balance of Fe and inevitable impurities.

12. A method for producing ferritic heat-resistant steel of any one of claims 1 to 4, which comprises heating steel at a temperature not lower than 1250°C, subjecting it to plastic working, such as forging, rolling or the like, then immediately keeping it at a temperature falling between 1000 and 1150°C for 1 hour or longer, and thereafter rapidly cooling it to a temperature not higher than its martensitic transformation-finishing point thereby making it have a martensitic texture, and then heating and tempering it at a temperature falling between 650 and 800°C.
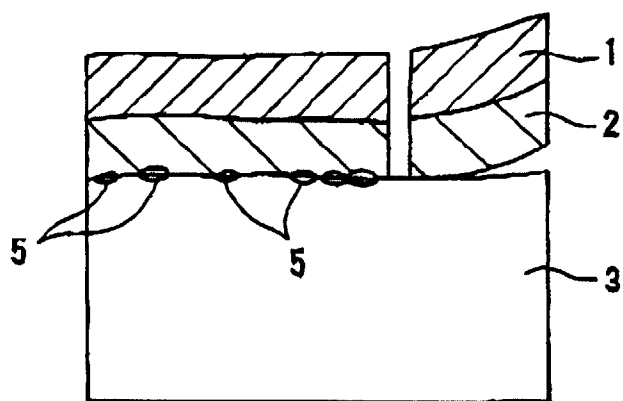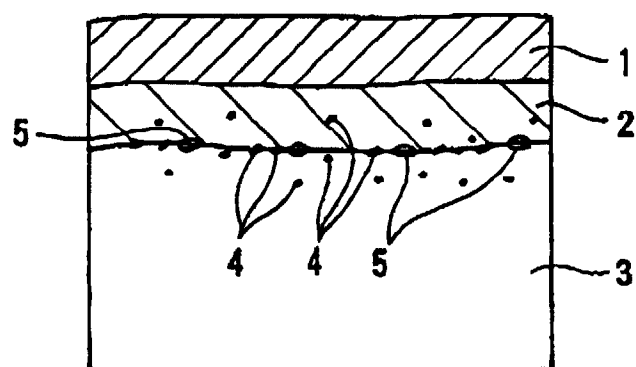
Fig. 1
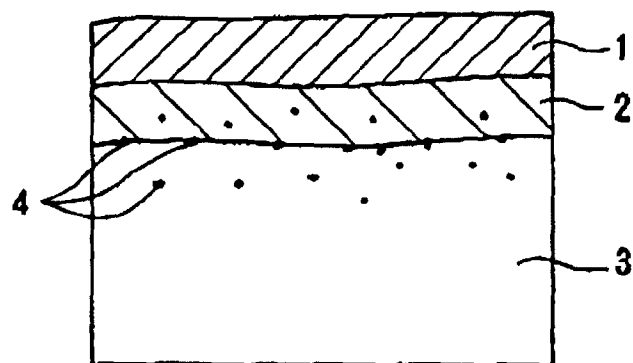
Fig. 2A

Fig. 2B

European Patent
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EUROPEAN SEARCH REPORT

Application Number

EP 98 30 7629

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
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