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

Ferritischer,wärmebeständiger Stahl und Verfahren zur Herstellung

Acier ferritique réfractaire et procédé de fabrication

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Description

FIELD OF THE INVENTION

[0001] The present invention relates to ferritic heat-resistant steel. 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. 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.

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-temperature 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 forms 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 having good steam oxidation-resistance and high long-term creep strength, which comprises by weight from 0.06 to 0.18 % of C, from 0 to 1.0 % of Si, from 0.05 to 1.5 % of Mn, not larger than 0.030 % of P, not larger than 0.05 % 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 0.02 to 0.14 % of Nb, from 0.10 to 0.50 % of V, from 0 to 0.10 % of N, from 0 to 0.01 % of B, not larger than 0.010 % of O, and from 0 to 0.050 % 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.

[0013] The invention further provides the following:

Ferritic heat-resistant steel of claim 1, which contains at least one of Rh and Ir in an amount by weight of from 0.3 to 5.0 % or Rh and from 0.6 to 5.0 % of Ir and in a ratio of $0.3\ \% \leq Rh + (1/2)Ir \leq 5.0\%$, as in claim 2; and
Ferritic heat-resistant steel of claim 1 or 2, 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 3.

BRIEF DESCRIPTION OF THE DRAWINGS

[0014]

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.
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.

[0015] 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

[0016] 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.

[0017] 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.

[0018] 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) 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.

[0019] 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.

[0020] The constitution of the invention is described in more detail hereinunder.

<Oxide Precipitates>

[0021] 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.

[0022] 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 base, so that they act as a barrier to the film peeling propagation in the film/base interface while preventing the film from swelling up.

[0023] The scale peeling-preventing effect of the invention could be interpreted as follows:

[0024] In the invention, 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.

[0025] 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.

[0026] 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>

[0027] (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 %.

[0028] 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.

[0029] (2) 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 %.

[0030] (3) 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 %.

[0031] (4) 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%.

[0032] (5) 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%.

[0033] (6) 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%.

[0034] (7) 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 0.14%.

[0035] (8): 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%.

[0036] (9) 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 %.

[0037] (10) 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 have now been found to be effective. In the present invention Rh and Ir are 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 %.

[0038] (11) 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.

[0039] (12) 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..

[0040] (13) 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%.

[0041] 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 peeling 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.

[0042] 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>

[0043] 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 A_1 transformation point of steel thereby lowering the temper softening resistance of steel.

[0044] 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.

[0045] As a result, the long-term creep strength of the steel at high temperatures higher than 630°C is greatly increased, and the steel shall have excellent long-term creep strength.

<Steam Oxidation Resistance>

[0046] 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.

[0047] 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.

[0048] 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 $0.3\ \% \leq Rh + (1/2)\ Ir \leq 5.0\ \%$, in which % being by weight, in view of their ability to exhibit and saturate the effect.

[0049] The ferritic heat-resistant steel of the invention can be produced in any ordinary equipment and process generally employed in the prior art.

[0050] 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.

[0051] 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 slab-making 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.

[0052] 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.

[0053] 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

[0054] Various types of steel each having the chemical composition shown in Table 1 below were produced in a vacuum high-frequency induction furnace having a capacity for 10 kg steel.

Table 1

		C	Si	Mn	W	Mo	W+2Mo	Nb	V	N	Others
		P	S	Cr	Rh	Ir	Rh + (1/2) Ir	B	O	Sol. Al	
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	

[0055] 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.

[0056] Samples Nos. 1 to 6 of the invention in Table 1 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.

[0057] On the other hand, Comparative Samples 1 and 2 in Table 1 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.

[0058] 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]

[0059] 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]

[0060] 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 Piece:	1000 hours
Measured Matter:	Thickness of scale formed

[0061] The data obtained in those tests are shown in Table 2.

Table 2

		Time before Creep Rupture (hrs) 650°C, 140MPa	Time before Creep Rupture (hrs) 700°C, 120MPa	Mean Thickness of Scale Formed in Steam Oxidation (μm) 700°C x 1000 h
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

[0062] As in Table 2, 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.

[0063] 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 2. 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.

[0064] 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.

Claims

1. Ferritic heat-resistant steel having good steam oxidation-resistance and high long-term creep strength, which comprises by weight from 0.06 to 0.18 % of C, from 0 to 1.0 % of Si, from 0.05 to 1.5 % of Mn, not larger than 0.030 % of P, not larger than 0.05 % 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 0.02 to 0.14 % ofNb, from 0.10 to 0.50 % of V, from 0 to 0.10 % of N, from 0 to 0.01 % of B, not larger than 0.010 % of O, and from 0 to 0.050 % 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.

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

3. Ferritic heat-resistant steel as claimed in claim 1 or 2, of which the lath structure is made fine and the martensite phase is reinforced by at least one of Rh and Ir added thereto.

Patentansprüche

1. Ferritischer, wärmebeständiger Stahl mit guter Beständigkeit gegen Wasserdampf-Oxidation und hoher Langzeit-Kriechfestigkeit, umfassend 0,06 bis 0,18 Gew.-% C, 0 bis 1,0 Gew.-% Si, 0,05 bis 1,5 Gew.-% Mn, höchstens 0,030 Gew.-% P, höchstens 0,05 Gew.-% S, 8,0 bis 13,0 Gew.-% Cr, 0 bis 4,0 Gew.-% W, 0 bis 2,0 Gew.-% Mo, mit der Maßgabe, dass W + 2 Mo ≤ 4,0 Gew.-%, 0,02 bis 0,14 Gew.-% Nb, 0,10 bis 0,50 Gew.-% V, 0 bis 0,10 Gew.-% N, 0 bis 0,01 Gew.-% B, höchstens 0,010 Gew.-% O und 0 bis 0,050 Gew.-% lösliches Al; Rh und/oder Ir in einer Gesamtmenge von 0,3 bis 5,0 Gew.-%; und eine Differenzmenge auf 100 Gew.-% an Fe und unvermeidlichen Verunreinigungen.

2. Ferritischer, wärmebeständiger Stahl nach Anspruch 1, enthaltend Rh und/oder Ir in einer Menge von 0,3 bis 5,0 Gew.-% Rh und 0,6 bis 5,0 Gew.-% Ir und in einem Verhältnis von 0,3 Gew.-% ≤ Rh+(1/2) Ir ≤ 5,0 Gew.-%.

3. Ferritischer, wärmebeständiger Stahl nach Anspruch 1 oder 2, worin durch Zugabe von Rh und/oder Ir die Lattenstruktur verfeinert und die Martensitphase verfestigt ist.

Revendications

1. Acier ferritique réfractaire ayant une bonne résistance à l'oxydation à la vapeur et une résistance au fluage à long terme élevée, qui comprend en poids de 0,06 à 0,18 % de C, de 0 à 1,0 % de Si, de 0,05 à 1,5 % de Mn, pas plus de 0,030 % de P, pas plus de 0,05 % de S, de 8,0 à 13,0 % de Cr, de 0 à 4,0 % de W, de 0 à 2,0 % de Mo, pour autant que W + 2Mo ≤ 4,0 %, de 0,02 à 0,14 % de Nb, de 0,10 à 0,50 % de V, de 0 à 0,10 % de N, de 0 à 0,01 % de B, pas plus de 0,010 % de O, et de 0 à 0,050 % d'Al soluble, au moins un des Rh et Ir en une quantité totale de 0,3 à 5,0 %, et le restant en Fe et impuretés occasionnelles.

2. Acier ferritique réfractaire suivant la revendication 1, qui contient au moins un des Rh et Ir en une quantité en poids de 0,3 à 5,0 % de Rh et de 0,6 à 5,0 % de Ir et dans un rapport de 0,3 % ≤ Rh + (1/2) Ir ≤ 5,0 %.

3. Acier ferritique réfractaire suivant l'une ou l'autre des revendications 1 et 2, dont la structure en lattis est rendue fine et la phase martensitique est renforcée en y ajoutant au moins un des Rh et Ir.

Fig. 1

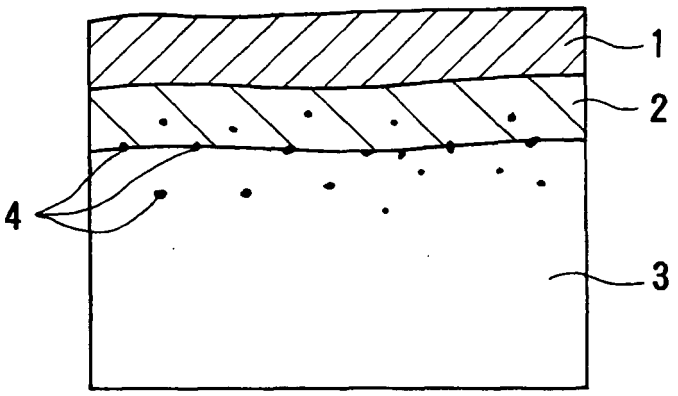


Fig. 2A

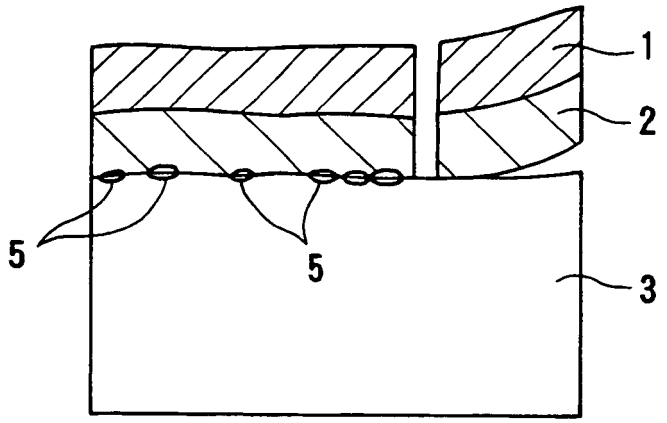


Fig. 2B

