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

(11) **EP 1 867 745 B1**

# (12) EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention
of the grant of the patent:
**06.08.2014 Bulletin 2014/32**

(21) Application number: **06731263.7**

(22) Date of filing: **06.04.2006**

(51) Int Cl.:
***C22C 38/02*** $^{(2006.01)}$ ***C22C 38/04*** $^{(2006.01)}$
***C22C 38/22*** $^{(2006.01)}$ ***C22C 38/24*** $^{(2006.01)}$

(86) International application number:
**PCT/JP2006/307315**

(87) International publication number:
**WO 2006/109664 (19.10.2006 Gazette 2006/42)**

## (54) FERRITIC HEAT-RESISTANT STEEL

FERRITISCHER HITZEBESTÄNDIGER STAHL

ACIER FERRITIQUE RESISTANT A LA CHALEUR

(84) Designated Contracting States:
**DE DK FR GB IT**

(30) Priority: **07.04.2005 JP 2005111149**

(43) Date of publication of application:
**19.12.2007 Bulletin 2007/51**

(73) Proprietor: **Nippon Steel & Sumitomo Metal Corporation**
**Tokyo 100-8071 (JP)**

(72) Inventors:
- **YOSHIZAWA, Mitsuru Sumitomo Metal Industries Ltd**
  **Osaka-shi, Osaka 5410041 (JP)**
- **IGARASHI, Masaaki Sumitomo Metal Industries Ltd**
  **Osaka-shi, Osaka 5410041 (JP)**
- **MIYAHARA, Mitsuo Sumitomo Metal Industries Ltd**
  **Osaka-shi, Osaka 5410041 (JP)**
- **NOGUCHI, Yasutaka Sumitomo Metal Industries Ltd**
  **Osaka-shi, Osaka 5410041 (JP)**

(74) Representative: **TBK**
**Bavariaring 4-6**
**80336 München (DE)**

(56) References cited:
**JP-A- 09 071 846**
**JP-A- 2000 301 377**
**JP-A- 2001 279 391**
**JP-A- 2002 363 709**
**US-A1- 2001 035 235**
**JP-A- 2000 248 337**
**JP-A- 2001 192 781**
**JP-A- 2002 363 709**
**US-A- 5 997 806**

Note: Within nine months of the publication of the mention of the grant of the European patent in the European Patent Bulletin, any person may give notice to the European Patent Office of opposition to that patent, in accordance with the Implementing Regulations. Notice of opposition shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

Printed by Jouve, 75001 PARIS (FR)

## Description

[Technical Field]

**[0001]** The present invention relates to ferritic heat resistant steel. More specifically, it relates to ferritic heat resistant steel excellent in high-temperature long-term creep strength and creep-fatigue strength. The heat resistant steel of the invention is suited for use as heat exchanger tubes, steel plates for pressure vessels, turbine members and the like which are used under high-temperature and high-pressure environments in boilers, nuclear power plant facilities, chemical industry facilities and so forth.

[Background of the Invention]

**[0002]** Heat resistant steels used in high-temperature and high-pressure environments in boilers, nuclear power plant facilities, chemical industry facilities and the like are generally required to have high-temperature creep strength, creep-fatigue strength, corrosion resistance and oxidation resistance.

**[0003]** High-Cr ferritic steels are superior in strength and corrosion resistance at temperatures of 500 to 650°C in low alloy steels. Further, high-Cr ferritic steels are high in thermal conductivity and low in thermal expansion coefficient, hence superior in thermal fatigue resistance characteristics to austenitic stainless steels; they are further characterized by their being inexpensive. They also have many further advantageous features; for example, they hardly cause scale peeling and are resistant to stress corrosion cracking.

**[0004]** In the latter half of the 1980s to the 1990s, the ASME P91 steel was put into practical use as a high-strength ferritic heat resistant steel and since then has been used in supercritical pressure boilers operated at steam temperatures of 566°C or higher. Further, in recent years, the ASME P92 steel has increased in creep strength and has been put into practical use in ultra supercritical pressure boilers operated at steam temperatures of about 600°C.

**[0005]** Currently, the reduction in $CO_2$ discharge has been demanded for the protection of the environment. For that purpose, it is required that the boilers in thermal power plants be operated at higher temperatures and higher pressures. Even in the case of the ASME P92 steel currently in practical use, thicker members made thereof are required for use in a higher temperature range, for example at about 630°C.

**[0006]** In thermal power plants, starting and stopping are repeated frequently and, therefore, it is important that thick members in particular, be excellent in creep-fatigue strength. Compared with the ASME P91 steel, the ASME P92 steel is markedly higher in creep strength but is parallel thereto in creep-fatigue strength. In order to operate boilers at higher temperatures and higher pressures, it is essential to improve the creep-fatigue strength of the ASME P92 steel.

**[0007]** Patent Documents 1 and 2 disclose inventions relating to a heat resistant steel containing 8 to 14% of Cr. Further, Patent Document 3discloses an invention concerning a heat resistant steel containing 8 to 13% of Cr. However, the inventions disclosed in these documents are not intended to improve the creep-fatigue strength of the heat resistant steels. The steels of these inventions may contain Nd (neodymium) but are not intended to utilize the effective function of Nd inclusions.

[Patent Document 1] Japan Patent Unexamined Publication No.2001-192781
[Patent Document 2] Japan Patent Unexamined Publication No.2002-224798
[Patent Document 3] Japan Patent Unexamined Publication No. 2002-235154

**[0008]** JP2002363709 (A) discloses a high Cr ferritic heat resistant steel which has remarkably improved creep ductility at a high temperature for a long time while maintaining strength at a high temperature for a long time creep. The heat resistant steel has a composition containing 0.05 to 0.15% C, ≤1% Si, ≤2% Mn, ≤0.03% P, ≤0.02% S, 8 to 15% Cr, 0.05 to 0.5% V, 0.002 to 0.18% Nb, 0.1 to 5% W, 0.01 to 1.5% Ni, 0.01 to 3% Cu, 0.0001 to 0.02% B, 0.0005 to 0.05% sol. Al and 0.0005 to 0.1% N, and further containing one or more kinds selected from 0.0001 to 0.02% Ca and 0.0001 to 0.02% Mg, and Nd in an amount simultaneously satisfying the following inequalities (1) and (2), and the balance Fe with impurities: $2(Nd/144)>(S/32)/2+(P/31)/30-(Ca/40)-(Mg/24)$ (1), and $3(Nd/144)>(Ca/40)+(Mg/24)$ (2).

[Disclosure of Invention]

[Problems to be Solved by the Invention]

**[0009]** It is an objective of the present invention to provide a ferritic heat resistant steel excellent in high-temperature long-term creep strength as well as in creep-fatigue strength.

[Means for Solving the Problems]

**[0010]** Fig. 1 is a depiction showing typical examples of the strain wave form in creep-fatigue testing. The one shown in Fig. 1 (a) is the PP type (fast-fast) strain wave form imposing strains at a high speed so that no creep strains may be placed either on the tensile side or on the compressive side. The one shown in Fig. 1 (b) is the CP type (slow-fast) strain wave form. This is a wave form imposing strains at a low speed on the tensile side and at a high speed on the compressive side in order to introduce the tensile creep strains.

**[0011]** When the life of the PP type strain wave form mentioned above is compared with the life of the CP type strain wave form, the life of the CP type strain wave form causing creep damages is shorter. Generally, the lives of heat resistant steels used in boilers, nuclear power plants and chemical plants under high-temperature and high-pressure environments are estimated by carrying out a creep-fatigue test in the total strain range of 0.4 to 1.5%.

**[0012]** Since such boilers and other facilities as mentioned above are used at high temperatures and at high pressures for a long period of time, therefore the members thereof are placed under creep strains and accept loads of the CP type. In order to ensure the creep-fatigue life of each member of a facility actually used in high-temperature and high-pressure conditions, a structure capable of reducing the generated strains is generally employed. Therefore, when high-Cr ferritic steels are used in those facilities, it is necessary that they have a reliable creep-fatigue life in the low-strain region, namely a total strain range of about 0.5%, within the entire strain range of 0.4 to 1.5% used in the above-mentioned creep-fatigue test under the CP type strain wave form.

**[0013]** The $10^5$ hour creep strengths at 600°C of the ASME P91 and P92 steels mentioned above are about 98 MPa and 128 MPa, respectively; therefore the P92 steel is higher in strength. However, creep-fatigue testing performed at 600°C in the total strain range of 0.5% under the CP type strain wave form shown in Fig. 1 revealed that, in each case, there is no great difference in the life compared with the case of about 3000 cycles. Thus, the results obtained indicate that, in spite of it’s showing an improvement in creep strength as compared with the P91 steel, the P92 steel shows no improvement in creep-fatigue strength. These results suggested that the P92 steel involve some cause for an incapability of improving the creep-fatigue strength thereof or, in other words, some cause for decreasing creep-fatigue strength. Therefore, the present inventors made intensive investigations in an attempt to improve the creep-fatigue strength of the P92 steel.

**[0014]** First, investigations were made concerning the influences of minute amounts of δ ferrite resulting from the segregation of alloying elements which is considered to be a cause for failure to improve creep-fatigue strength.

(a) Investigations of the influence of δ ferrite

**[0015]** The P92 steel contains, in addition to the components contained in the conventional 9Cr ferritic heat resistant steels, large amounts of ferrite-forming elements (Mo, W, Nb, V, etc.). Therefore, there is the possibility that very slight amounts of δ ferrite remain at the grain boundary interfaces. In order to completely eliminate δ ferrite, materials that added each of minute amounts of the Cu, Ni or Co (these being austenite-forming elements) to the P92 steel were prepared and their creep-fatigue strengths were compared. The test temperature was 600°C and the total strain range was 0.5%. As a result, the life was about 1600 to 2100 cycles, which slightly decreased compared with the P92 steel.

**[0016]** The above results revealed that the failure in improving the creep-fatigue strength of the P92 steel is not due to δ ferrite but is due to the excessive contents of austenite-forming elements which lead to decreases in creep-fatigue strength.

**[0017]** Then, the investigation described below under (b) was carried out in order to reveal the contribution of the grain boundaries to the creep-fatigue strength.

(b) Investigation of the effect of the prior austenite grain size on the creep-fatigue strength of the P92 steel

**[0018]** The P92 steel was treated at a normalization temperature of 1050°C or 1200°C to alter the prior austenite grain size to about 25 μm or 125 μm. The steel was then thermally refined by tempering so that the tensile strength might amount to about 710 MPa, and then subjected to creep-fatigue testing. The test temperature was 600°C and the total strain range was 0.5%.

**[0019]** As a result of the above test, the life at the ordinary grain size of 25 μm was about 3000 cycles while the life of the steel in a coarse grain condition, namely at a grain size of 125 μm, was about 2300 cycles. From this, it was revealed that in the case of the coarse-grained steel, the creep-fatigue life thereof is shorter even if it is parallel in strength to the fine-grained steel.

(c) The reason why the coarse-grained steel is higher in creep-fatigue strength

**[0020]** The reason why the coarse-grained steel is higher in creep-fatigue strength as indicated by the test results given above under (b), was examined.

**[0021]** Generally, it is understood that the high-temperature creep characteristics tend to be superior in the case of coarser grains. Therefore, the samples used in the above test (b) were examined for creep strength at 600°C and 160 MPa. As a result, the rupture time of the sample with a grain size of 25 μm was about 6000 hours, whereas the time for rupture of the sample with a grain size of 125 μm was about 9000 hours; the creep strength is higher in the case of coarser grains as traditionally stated. These results revealed that improvements in the creep-fatigue strength of fine-grained steels couldn't be explained in terms of tensile strength and creep strength.

**[0022]** Fine-grained steel has an increased grain boundary area. It is supposed that as the grain boundary area increases, the segregation of such impurity elements as P, S, As and Sn, in particular S, is suppressed. Therefore, the segregation of S at grain boundaries was examined.

**[0023]** Ferritic heat resistant steels generally contain about 0.001% of S as an impurity. On the industrial product level, it is difficult to reduce the level of S to a level lower than 0.001%. In laboratory production as well, contamination with S due to alloying elements is inevitable and it is difficult to eliminate the phenomenon of segregation by reducing S by melting in conventional methods of steel production.

**[0024]** Temper embrittlement is generally known as a phenomenon caused by segregation of S. Temper embrittlement results when martensite is tempered in a certain temperature range around 600°C and a minute amount of Mo is known to be effective in reducing that phenomenon.

**[0025]** If the phenomenon of creep-fatigue is in correlation with the segregation of S, there is also presumably a certain correlation between the Mo content and creep-fatigue characteristics. Therefore, creep-fatigue strength examinations (test temperature: 600°C, total strain range 0.5%) were made at varied Mo content levels, namely 0.01%, 0.07%, 0.13%, 0.33% and 1.83%. As a result, when the Mo content was 0.13% or 0.33%, the life was about 3000 cycles, whereas, at low Mo content levels (0.01% and 0.07%), the creep-fatigue strength decreased to about 2000 cycles. This revealed that the Mo content makes a certain contribution to the creep-fatigue strength. When the Mo content was further increased to 1.83%, the creep-fatigue life was about 2500 cycles and a tendency to deteriorate was observed in the fatigue characteristics.

**[0026]** Thereafter, the occurrence of S in the steel was studied. As a result, it was revealed that S occurs in the form of MnS, as shown in Fig. 2. If S trapped as MnS is liberated and segregates at grain boundaries during high-temperature creep-fatigue testing, this S will presumably exert adverse influences on the creep-fatigue characteristics.

(d) Fixation of S

**[0027]** If the segregation of the liberated S produces adverse influences on the creep-fatigue characteristics, as mentioned above, it is expected that the creep-fatigue strength may possibly be increased by incorporating, in addition to Mn, an element capable of more firmly trapping S.

**[0028]** Therefore, the influences on the creep-fatigue strength of Ca, Mg, Nd, La and Ce, which can possibly form sulfides, were investigated.

**[0029]** As a result, it was revealed that when Nd was incorporated at a level of 0.025%, the Nd inclusions immobilize S in addition to MnS. The Nd inclusions mean "Nd oxide" and "composite inclusions comprising Nd oxide and Nd sulfide". The "composite inclusions comprising Nd oxide and Nd sulfide" fix S directly. On the other hand, "Nd oxide" also fixes S indirectly as a result of the segregation of S around the "Nd oxide". A "composite inclusion comprising Nd oxide and Nd sulfide" observed in a Nd-containing steel is shown in Fig. 3 as an example of the Nd inclusion.

**[0030]** A steel containing Nd, which can fix S directly and indirectly, as mentioned above, was subjected to creep-fatigue testing under the conditions mentioned above, namely at a test temperature of 600°C and in a total strain range of 0.5%, and it was revealed that the fatigue life was markedly increased, namely to about 7000 cycles.

**[0031]** While the creep-fatigue lives (test temperature 600°C, total strain range 0.5%) of steels containing Ca, Mg, La or Ce singly were about 3000 to 4000 cycles, the lives of steels containing the above component together with Nd were 6000 to 7000 cycles; it was thus revealed that marked improvements in creep-fatigue life are attainable in that manner.

(e) Addition of Nd in combination with Cu, Ni or Co

**[0032]** As described above under (a), steels containing a minute amount of the austenite-forming element Cu, Ni or Co showed a tendency toward decreases in creep-fatigue strength. For further clarifying this phenomenon, steels resulting from addition of a minute amount of Cu, Ni or Co to a steel containing a minute amount of Nd were subjected to creep a fatigue life evaluation.

**[0033]** As a result, it was revealed that the steel containing Nd, in combination with a minute amount of Cu, Ni or Co, showed a creep-fatigue life of about 4000 cycles and thus improved in creep-fatigue characteristics, as compared with the steel containing no Nd but, when compared with the steel containing only Nd, the creep-fatigue life was markedly inferior.

**[0034]** The following conclusions can be deduced from the above investigations.

(1) Mo at levels of 0.1% or higher contributes to the creep-fatigue characteristics.
(2) S is mostly found fixed as MnS, but when part of S is liberated during high-temperature fatigue testing and segregates at grain boundaries the creep-fatigue strength decreases.
(3) Addition of Nd and immobilizing S by Nd oxide or in the form of composite inclusions comprising Nd oxide and Nd sulfide and further immobilizing S partly as MnS, it becomes possible to markedly improve the creep-fatigue strength. That effect is significant when the Nd inclusion density is not lower than 10000/mm$^3$. The "Nd inclusions" is a term collectively referring to the above-mentioned "Nd oxide" and "composite inclusions comprising Nd oxide and Nd sulfide".
(4) The austenite-forming elements such as Cu, Ni and Co cause decreases in creep-fatigue strength. It is also possible to observe this tendency with steels further containing Nd in minute amounts. Such phenomenon is presumably caused by the promotion, by Cu, Ni and Co, of the phenomenon of S fixed as MnS being liberated during creep-fatigue testing.

**[0035]** The gist of the present invention, which has been made based on the above-mentioned investigation results, consists in the following heat-resistant steel. In the following, "%" used in relation to the content of each component means "% by mass".

(1) Ferritic heat-resistant steel which comprises C: 0.01 to 0.13%, Si: 0.15 to 0.50%, Mn: 0.2 to 0.5%, P: not higher than 0.02%, S; not higher than 0.005%, Cr: exceeding 8.0% but lower than 12.0%, Mo: 0.1 to 1.5%, W: 1.0 to 3.0%, V: 0.1 to 0.5%, Nb: 0.02 to 0.10%, sol. Al: not higher than 0.015%, N: 0.005 to 0.070%, Nd: 0.005 to 0.050% and B: 0.002 to 0.015%, optionally further contains one or more elements selected among Ta: not higher than 0.04%, Hf: not higher than 0.04%, Ti: not higher than 0.04%, Ca: not higher than 0.005% and Mg: not higher than 0.005%, with the balance Fe and impurities, wherein the content of Ni is lower than 0.3%, the content of Co is lower than 0.3% and the content of Cu is lower than 0.1%, the total content of rare earth elements, except for Nd, is preferably not higher than 0.04% among the impurities, said steel containing Nd inclusions with a diameter of 0.3 to 1 μm consisting of Nd oxide and composite inclusions comprising Nd oxide and Nd sulphide at a Nd inclusion density of not lower than 10000/mm$^3$.
(2) Ferritic heat-resistant steel according to (1) above, which is characterized in that the creep-fatigue life thereof, under the CP type strain wave form at 600°C, under the conditions of a strain rate of 0.01%/sec on the tensile side, a strain rate of 0.8%/sec on the compressive side and a total strain range of 0.5% is, not shorter than 5000 cycles.

[Brief Description of the Drawings]

**[0036]**

[Fig. 1] Fig. 1 is a depiction of typical examples of the strain wave form in creep-fatigue testing.
[Fig. 2] Fig. 2 is an illustration showing a sulfide observed in the ASME P92 steeL
[Fig. 3] Fig. 3 is an illustration showing a "composite inclusion comprising Nd oxide and Nd sulfide" as observed in a Nd-containing steel.

[Best Modes for Carrying out the Invention]

1. Chemical composition

**[0037]** First, the effects of the components constituting the heat-resistant steel of the invention and the reasons for restricting the contents thereof are explained.

C: 0.01 to 0.13%

**[0038]** C serves as an austenite-stabilizing element and stabilizes the structure of the steel. It also forms carbides MC or carbonitrides M(C, N) in order to contribute improvements in creep strength. M in the MC and M(C, N) indicates an alloying element. At levels lower than 0.01%, however, the above-mentioned effects of C will not be obtained to a satisfactory extent; in some cases, it may cause an increase in the amount of δ ferrite, leading to a decrease in strength. On the other hand, at C content levels exceeding 0.13%, the workability and/or weldability will deteriorate and, in addition, coarsening of carbides will occur from the early stage of use, causing decreases in long-term creep strength. Therefore, it is necessary to restrict the C content to 0.13% or lower. A more desirable lower limit and a more desirable upper limit are 0.08% and 0.11%, respectively.

Si: 0.15 to 0.50%

**[0039]** Si is contained as a steel-deoxidizing element and is also an element necessary for increasing the steam oxidation resistance performance. The lower limit is set at 0.15% at which the steam oxidation resistance performance will not be impaired. On the other hand, when the Si content exceeds 0.50%, the decrease in creep strength is remarkable and, therefore, the upper limit is set at 0.50%. In particular when the vapor oxidation resistance requires, it is desirable that the lower limit to the Si content be set at 0.25%.

Mn: 0.2 to 0.5%

**[0040]** Mn contributes as a deoxidizing element and an austenite-stabilizing element. Further, it forms MnS and thus immobilizes S. For obtaining such effects, the content thereof is required to be not lower than 0.2%. On the other hand, at levels exceeding 0.5%, decreases in creep strength may be caused. Therefore, the appropriate content of Mn is 0.2 to 0.5%. Amore preferred lower limit is 0.3%.

P: not higher than 0.02%, S: not higher than 0.005%

**[0041]** P and S, which are impurities, deteriorate the hot workability, weldability, creep strength and creep-fatigue strength of the steel, and, therefore, their contents are desirably as low as possible. Since, however, excessive purification of the steel results in marked increases in cost of production, the allowable upper limit is set at 0.02% for P and 0.005% for S.

Cr: exceeding 8.0% but lower than 12.0%

**[0042]** Cr is an element essential for securing the high-temperature corrosion resistance and oxidation resistance of the steel of the invention, in particular the steam oxidation resistance characteristics. Further, Cr forms carbides and improves the creep strength. In order to obtain such effects, it is necessary that the content thereof be above 8.0%. Excessively high contents thereof, however, cause decreases in long-term creep strength and, therefore, the upper limit is set at 12.0%. A more preferred lower limit is 8.5%, and a more preferred upper limit is lower than 10.0%.

Mo: 0.1 to 1.5%

**[0043]** Mo serves as an element for solid solution hardening and contributes to improvements in creep strength. Further, as a result of a detailed investigation concerning the correlation between the Mo content and creep-fatigue strength, it was revealed that 0.1% or higher levels of Mo contribute to improvements in creep-fatigue characteristics and levels thereof exceeding 1.5% cause decreases in long-term creep strength. Therefore, a proper content of Mo is 0.1 to 1.5%. A more preferred lower limit and a more preferred upper limit are 0.3% and 0.5%, respectively.

W: 1.0 to 3.0%

**[0044]** W serves as an element for solid solution hardening and contributes to improvements in creep strength. Further, it is partly dissolved in Cr carbides and prevents coarsening of the carbides and thus contributes to improvements in creep strength. However, at levels lower than 1.0%, such effects are not significant. On the other hand, at W levels exceeding 3.0%, the formation of $\delta$ ferrite is promoted, causing decreases in creep strength. Therefore, a proper range of the W content is 1.0 to 3.0%. A more preferred lower limit is at a level exceeding 1.5%, and a more preferred upper limit is 2.0%.

V: 0.1 to 0.5%

**[0045]** V contributes to improvements in creep strength owing to its solid solution hardening effect and also owing to its formation of fine carbonitrides. For obtaining this effect, it is necessary that the content thereof be not lower than 0.1%. On the other hand, at V content levels exceeding 0.5%, it promotes the formation of $\delta$ ferrite and thus causes decreases in creep strength. Therefore, the upper limit should be set at 0.5%. A more preferred lower limit and a more preferred upper limit are 0.15% and 0.25%, respectively.

Nb: 0.02 to 0.10%

**[0046]** Nb forms fine carbonitrides and contribute to improvements in long-term creep strength. For obtaining this effect, a content of not lower than 0.02% is necessary. However, at excessive content levels thereof, it promotes the formation of δ ferrite, causing decreases in long-term creep strength. Therefore, a proper content of Nb is 0.02 to 0.10%. A more preferred lower limit and a more preferred upper limit are 0.04% and 0.08%, respectively.

sol. Al: not higher than 0.015%

**[0047]** Al is used as a deoxidizing agent for molten steel. At levels exceeding 0.015%, however, it causes decreases in creep strength and, therefore, the upper limit should be set at 0.015% or lower. A more preferred upper limit is 0.010%.

N: 0.005 to 0.070%

**[0048]** N is effective as an austenite-stabilizing element, like C. N also precipitates out nitrides or carbonitrides and thus improves the high-temperature strength of the steel. For obtaining such effect, a content of not lower than 0.005% is necessary. On the other hand, at excessive N content levels, it may cause the formation of blow holes in the step of melting or cause weld defects and, in addition, may cause decreases in creep strength due to coarsening of nitrides and carbonitrides. Therefore, the upper limit to the N content should be set at 0.070%. A more preferred lower limit to the N content is 0.020%.

Nd: 0.005 to 0.050%

**[0049]** Nd markedly improves the creep-fatigue strength, as mentioned hereinabove. For obtaining that effect, a content of not lower than 0.005% is necessary. At levels exceeding 0.050%, however, it forms coarse nitrides, causing decreases in creep strength. Therefore, the upper limit should be set at 0.050%. A more preferred upper limit is 0.040%.

B: 0.002 to 0.015%

**[0050]** B increases the hardenability and plays an important role in securing the high-temperature strength. Such effects become significant at levels of 0.002% or higher. At levels exceeding 0.015%, however, it causes decreases in weldability and long-term creep strength.

Ni: lower than 0.3%, Co: lower than 0.3%, Cu: lower than 0.1%

**[0051]** These austenite-stabilizing elements lower the creep-fatigue strength even at low content levels, as mentioned hereinabove. In some instances, however, minute amounts of Ni, Co and Cu may be inevitably mixed in from raw materials to be melted. Therefore, in the practice of the invention, the Ni and Co contents are each suppressed to a level lower than 0.3% and the Cu content to a level lower than 0.1%. Within the above ranges, their adverse effects on the creep-fatigue strength are insignificant.

First group components: Ta, Hf and Ti

**[0052]** One or more of these components can be added according to need. When they are added, the respective proper addition levels are as descried below

Ta: not higher than 0.04%, Hf: not higher than 0.04%, Ti: not higher than 0.04%

**[0053]** Ta, Hf and Ti are incorporated in the steel to form fine carbonitrides and thereby contribute to improvements in creep strength. In order to maximize the effect, the content of each of them is desirably not lower than 0.005%. However, even when the content of each of them is higher than 0.04%, the effect is already at a point of saturation and such a high content may cause deteriorations in creep strength. Therefore it is recommended that an upper limit to the content of each of them be set at 0.04%.

Second group components: Ca and Mg

**[0054]** One or both of these components can be also added according to need. When they are added, the respective proper addition levels are as descried below

Ca: not higher than 0.005%, Mg: not higher than 0.005%

**[0055]** Both of these elements improve the hot workability of the steel. Therefore, when the hot workability of the steel is to be particularly improved, either or both of them could be added. Their effect becomes significant at levels of 0.0005% or higher and, therefore, a lower limit is desirably set at 0.0005% for each of them. However, if content levels exceed 0.005%, the creep strength decreases, so that the upper limit should be set at 0.005%.

Rare earth elements except for Nd: not higher than 0.04%

**[0056]** On the occasion of the incorporation of Nd, such rare earth elements as La and Ce may sometimes be mixed in as impurities. When, however, the total content of rare earth elements except for Nd is not higher than 0.04%, such characteristics as creep strength and creep ductility are not greatly influenced; hence, the content thereof up to 0.04% is allowable.

2. Nd inclusions

**[0057]** One of the characteristic features of the steel of the invention is that the steel should contain Nd inclusions at a density of not lower than 10000 inclusions/$mm^3$.

**[0058]** The Nd inclusions observed in the steel of the invention are "Nd oxide" and "composite inclusions comprising Nd oxide and Nd sulfide", as mentioned hereinabove. More specifically, they include $Nd_2O_3$, $Nd_2O_2S_4$, $Nd_2O_2SO_4$, $Nd_2O_2S$ and so forth.

**[0059]** The diameters of the Nd inclusions vary from about 0.3 $\mu$m to about 1 $\mu$m, and Nd inclusions are generally observed in steels containing a minute amount of Nd. However, in the case of steels containing Co, Ni and Cu abundantly, the amount of MnS is large and the content of Nd inclusions is markedly low. When the density of the Nd inclusions is lower than 10000 inclusions/$mm^3$, no improvements in creep-fatigue strength are observed. Therefore, the density of Nd inclusions must be not lower than 10000 inclusions/$mm^3$.

3. Method of production

**[0060]** The steel of the invention can be produced in a plant commonly used for industrial production. Thus, a steel having a chemical composition with specifications in accordance with the invention may be obtained by refining it in a furnace, such as an electric furnace or converter and adjusting the composition by means of deoxidation and adding alloying elements. In particular when strict composition adjustments are required, the molten steel may be subjected to an appropriate treatment, such as vacuum treatment, prior to the addition of the alloying elements.

**[0061]** The method of introducing Nd inclusions into the steel at a density of not lower than 10000/$mm^3$ is as follows. Sufficient deoxidation should be carried out beforehand using C, Si, Mn, Al and/or the like in the stage from the manufacture of pig iron to the manufacture of steel. Therefore, the high oxygen contents in the molten steel result in requiring more addition of Nd. Then, in the case of ingot casting, the composition, exclusive of Nd, is adjusted before casting ingots and, just prior to casting, Nd is added for the formation of the Nd inclusions. In the case of continuous casting, the composition, exclusive of Nd, is adjusted before the introduction of the molten steel into the tundish and then Nd is added to the tundish for the formation of Nd inclusions. By finally adjusting the Nd content only, it becomes possible to cause the formation of an appropriate amount of Nd inclusions. The thus cast slabs, billets or steel ingots are further processed into steel tubes/pipes, steel plates/ sheets and so forth.

**[0062]** In the case of manufacturing seamless pipes, billets may be extruded into the pipes, or subjected to piercing, using an inclined roll type piercer, to give the pipes, or subject the pipes to the Erhardt Push Bench Pipe Manufacturing process in order to manufacture large diameter forged pipes, for instance. In manufacturing steel pipes/tubes, it is also possible to make size adjustments by cold working according to need. The pipes or tubes produced are subjected to appropriate heat treatment, if necessary followed by shot peening, acid cleaning and/or like surface treatment.

**[0063]** The steel plates or sheets include hot-rolled and cold-rolled plates or sheets. Hot-rolled steel plates or sheets can be obtained by subjecting slabs to hot rolling, and cold-rolled steel plates or sheets can be obtained by subjecting the hot-rolled steel plates/sheets to cold rolling.

[Examples]

**[0064]** Steel species having the respective chemical compositions specified in Table 1 were produced by melting, using a vacuum induction melting furnace, and 50kg ingots with a diameter of 144 mm, were prepared from each steel species. The steels given the symbols A to M are the steels according to the present invention, and those given the symbols 1 to 22 are steels for comparison. The steels given the symbols A to M and the symbols 15 to 20 were sufficiently deoxidized with C, Si, Mn and Al and, then, Nd was added just prior to casting. In the steel having the symbol 21, Nd was added at the start of melting and, in the case of the steel having the symbol 22, deoxidation was carried out using only carbon and then Nd was added.

**[0065]** These ingots were subjected to hot forging and hot rolling to produce 20mm-thick plates, which were then maintained at a temperature of 1050°C for 1 hour and then air-cooled (AC). The plates were further tempered by maintaining the temperature at 760°C to 780°C for 3 hours, followed by air cooling (AC). Test specimens were taken from each of these plates so that the lengthwise direction of the test specimens might be identical to the direction of rolling. The test specimens were subjected to creep rupture testing, creep-fatigue testing and a Nd inclusion distribution examination under the conditions specified below.

(1) Creep rupture testing

**[0066]**

Test specimens: diameter 6.0 mm, gage length: 30 mm, test temperature: 600°C, applied stress: 160 MPa,
Test item: rupture time (h).

(2) Creep fatigue testing

**[0067]**

Test specimens: diameter 10 mm, gage length: 25 mm, test temperature: 600°C (in air)
Strain wave form: CP type strain wave form, total strain range $\Delta\varepsilon_t$ = 0.5%, strain rate: tensile side: 0.01%/sec, compressive side: 0.8%/sec
Test item: creep-fatigue life $N_f$ (cycles)

(3) Nd inclusion distribution examination

**[0068]** Test specimens were cut out from each material as hot-worked and, after polishing and etching, extracted replicas were prepared by vapor deposition of carbon and observed under an electron microscope at a magnification of 2000 and, at the same time, the inclusions were identified by on EDX analysis (energy dispersive X-ray analysis), and the number of Nd inclusions (inclusions/mm$^2$) were determined and the precipitate density (inclusions/mm$^3$) was calculated by raising the determined value to a three-second power. Observations were made for 10 fields and the mean of the 10 values was recorded as a precipitate density.

**[0069]** The results of the creep rupture testing, creep-fatigue testing and the Nd inclusion distribution examination of the various steels, are shown in Table 2.

**[0070]** [Table 1]

Table 1

| Symbol | Chemical corrosition (mass% Balance: Fe and impurities) | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | C | Si | Mn | P | S | Cr | Mo | W | V | Nb | sol.Al | N | Nd | B | Ni | Co | Cu | other |
| A | 0.10 | 0.33 | 0.46 | 0.016 | 0.001 | 8.65 | 0.42 | 1.95 | 0.19 | 0.059 | 0.003 | 0.044 | 0.025 | 0.0039 | - | - | - | |
| B | 0.10 | 0.39 | 0.44 | 0.019 | 0.001 | 9.28 | 0.31 | 1.99 | 0.20 | 0.060 | 0.004 | 0.053 | 0.009 | 0.0035 | - | - | - | |
| C | 0.09 | 0.34 | 0.39 | 0.015 | 0.002 | 8.87 | 0.38 | 1.77 | 0.19 | 0.047 | 0.006 | 0.056 | 0.018 | 0.0038 | - | - | - | |
| D | 0.10 | 0.20 | 0.43 | 0.018 | 0.001 | 8.42 | 0.48 | 1.86 | 0.19 | 0.067 | 0.005 | 0.065 | 0.013 | 0.0041 | - | - | 0.09 | |
| E | 0.10 | 0.17 | 0.33 | 0.019 | 0.001 | 9.19 | 0.47 | 1.82 | 0.17 | 0.058 | 0.005 | 0.055 | 0.033 | 0.0061 | 0.23 | - | - | |
| F | 0.11 | 0.36 | 0.49 | 0.019 | 0.002 | 9.03 | 0.44 | 1.97 | 0.21 | 0.070 | 0.006 | 0.040 | 0.027 | 0.0049 | - | 0.21 | - | |
| G | 0.09 | 0.18 | 0.42 | 0.013 | 0.001 | 8.91 | 0.31 | 1.77 | 0.20 | 0.067 | 0.007 | 0.057 | 0.027 | 0.0033 | - | - | - | Ti : 0.006 |
| H | 0.11 | 0.18 | 0.37 | 0.011 | 0.002 | 9.70 | 0.36 | 1.92 | 0.20 | 0.054 | 0.002 | 0.066 | 0.025 | 0.0064 | - | - | - | La: 0.02 |
| I | 0.09 | 0.34 | 0.37 | 0.010 | 0.001 | 8.56 | 0.34 | 1.88 | 0.21 | 0.066 | 0.006 | 0.056 | 0.016 | 0.0025 | - | - | - | Ce: 0.015 |
| J | 0.09 | 0.20 | 0.48 | 0.019 | 0.001 | 9.43 | 0.34 | 1.60 | 0.20 | 0.075 | 0.005 | 0.053 | 0.013 | 0.0047 | 0.12 | - | 0.08 | Ca: 0.002 |
| K | 0.10 | 0.39 | 0.44 | 0.018 | 0.001 | 9.73 | 0.37 | 1.56 | 0.18 | 0.048 | 0.004 | 0.067 | 0.019 | 0.0041 | - | 0.13 | - | Mg : 0.0035 |
| L | 0.10 | 0.32 | 0.37 | 0.014 | 0.001 | 9.26 | 0.41 | 1.60 | 0.17 | 0.061 | 0.004 | 0.061 | 0.028 | 0.0047 | - | - | - | Ta: 0.009 |
| M | 0.09 | 0.44 | 0.38 | 0.016 | 0.001 | 8.91 | 0.45 | 1.76 | 0.24 | 0.066 | 0.003 | 0.039 | 0.031 | 0.0044 | - | - | - | Hf : 0.03 |
| 1 | 0.10 | 0.25 | 0.41 | 0.015 | 0.002 | 9.13 | 0.89 | - | 0.20 | 0.064 | 0.002 | 0.043 | - | 0.0001 | - | - | - | |
| 2 | 0.10 | 0.26 | 0.36 | 0.010 | 0.001 | 8.92 | 0.33 | 1.73 | 0.20 | 0.057 | 0.008 | 0.049 | - | 0.0036 | - | - | - | |
| 3 | 0.11 | 0.42 | 0.38 | 0.012 | 0.001 | 9.35 | 0.40 | 1.74 | 0.19 | 0.066 | 0.007 | 0.059 | - | 0.0030 | - | - | 0.22 | |
| 4 | 0.10 | 0.33 | 0.32 | 0.017 | 0.001 | 8.81 | 0.36 | 1.59 | 0.21 | 0.058 | 0.004 | 0.056 | - | 0.0064 | 0.49 | - | - | |
| 5 | 0.09 | 0.25 | 0.32 | 0.015 | 0.002 | 8.86 | 0.35 | 1.55 | 0.22 | 0.049 | 0.003 | 0.063 | - | 0.0064 | - | 0.50 | - | |
| 6 | 0.09 | 0.43 | 0.44 | 0.015 | 0.001 | 9.01 | 0.13 | 1.57 | 0.23 | 0.065 | 0.006 | 0.042 | - | 0.0051 | - | - | - | |
| 7 | 0.10 | 0.26 | 0.49 | 0.015 | 0.001 | 8.86 | 0.01 | 1.77 | 0.20 | 0.061 | 0.006 | 0.062 | - | 0.0046 | - | - | - | |
| 8 | 0.11 | 0.34 | 0.43 | 0.012 | 0.001 | 8.53 | 0.07 | 1.82 | 0.18 | 0.057 | 0.004 | 0.048 | - | 0.0040 | - | - | - | |
| 9 | 0.10 | 0.34 | 0.32 | 0.014 | 0.001 | 9.26 | 1.83 | 1.70 | 0.19 | 0.056 | 0.006 | 0.037 | - | 0.0048 | - | - | - | |
| 10 | 0.11 | 0.44 | 0.35 | 0.013 | 0.001 | 8.36 | 0.32 | 1.88 | 0.21 | 0.066 | 0.008 | 0.047 | - | 0.0036 | - | - | - | La : 0.03 |
| 11 | 0.11 | 0.34 | 0.42 | 0.012 | 0.002 | 8.67 | 0.47 | 1.73 | 0.17 | 0.053 | 0.005 | 0.060 | - | 0.0064 | - | - | - | Ce : 0.025 |

(continued)

| Symbol | Chemical corrosition (mass% Balance: Fe and impurities) | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | C | Si | Mn | P | S | Cr | Mo | W | V | Nb | sol.Al | N | Nd | B | Ni | Co | Cu | other |
| 12 | 0.11 | 0.17 | 0.48 | 0.019 | 0.001 | 8.51 | 0.34 | 1.75 | 0.18 | 0.059 | 0.003 | 0.057 | - | 0.0064 | - | - | - | Ca : 0.0024 |
| 13 | 0.10 | 0.42 | 0.31 | 0.020 | 0.001 | 9.24 | 0.39 | 1.63 | 0.22 | 0.050 | 0.005 | 0.062 | - | 0.0049 | - | - | - | Mg : 0.0031 |
| 14 | 0.11 | 0.32 | 0.37 | 0.013 | 0.001 | 9.44 | 0.49 | 1.70 | 0.21 | 0.064 | 0.006 | 0.043 | 0.002 | 0.0047 | - | - | - | |
| 15 | 0.10 | 0.23 | 0.41 | 0.012 | 0.001 | 9.02 | 0.35 | 1.77 | 0.20 | 0.053 | 0.006 | 0.055 | 0.050 | 0.0052 | - | - | - | |
| 16 | 0.10 | 0.39 | 0.48 | 0.018 | 0.001 | 8.84 | 0.43 | 1.60 | 0.25 | 0.050 | 0.005 | 0.056 | 0.027 | 0.0047 | - | - | 0.19 | |
| 17 | 0.10 | 0.29 | 0.38 | 0.014 | 0.001 | 9.12 | 0.42 | 1.78 | 0.21 | 0.066 | 0.004 | 0.054 | 0.023 | 0.0043 | 0.53 | - | - | |
| 18 | 0.10 | 0.44 | 0.50 | 0.013 | 0.001 | 9.37 | 0.37 | 1.60 | 0.20 | 0.060 | 0.003 | 0.054 | 0.038 | 0.0043 | - | 0.52 | - | |
| 19 | 0.10 | 0.35 | 0.51 | 0.015 | 0.001 | 9.09 | 0.03 | 1.81 | 0.21 | 0.051 | 0.004 | 0.054 | 0.025 | 0.0053 | - | - | - | |
| 20 | 0.10 | 0.26 | 0.48 | 0.011 | 0.001 | 9.14 | 2.59 | 1.51 | 0.20 | 0.063 | 0.006 | 0.054 | 0.024 | 0.0049 | - | - | - | |
| 21 | 0.11 | 0.42 | 0.34 | 0.011 | 0.001 | 8.93 | 0.36 | 1.69 | 0.23 | 0.062 | 0.006 | 0.039 | 0.029 | 0.0039 | - | - | - | |
| 22 | 0.10 | 0.33 | 0.32 | 0.017 | 0.001 | 8.89 | 0.35 | 1.57 | 0.24 | 0.055 | 0.006 | 0.040 | 0.031 | 0.0044 | | - | - | |

**[0071]** [Table 2]

Table 2

| Symbol | Creep rupture time (hr) | Creep-fatigue life (cycle) | Nd inclusion | Note |
|---|---|---|---|---|
| A | 7092 | 6955 | 127476 | |
| B | 6280 | 5660 | 51941 | |
| C | 7806 | 7624 | 50444 | |
| D | 6661 | 5428 | 79161 | |
| E | 7745 | 5747 | 139727 | |
| F | 6840 | 5254 | 78571 | |
| G | 7831 | 6127 | 113590 | |
| H | 7006 | 6747 | 69146 | |
| I | 6399 | 6977 | 109778 | |
| J | 6279 | 5946 | 49007 | |
| K | 6715 | 6635 | 58781 | |
| L | 6904 | 5158 | 86908 | |
| M | 7259 | 5260 | 135225 | |
| 1 | 2115 | 3189 | 0 | ASME P91 |
| 2 | 6243 | 2960 | 0 | ASME P92 |
| 3 | 5542 | 2077 | 0 | |
| 4 | 4986 | 1625 | 0 | |
| 5 | 6915 | 1857 | 0 | |
| 6 | 6587 | 2927 | 0 | ASME P92 |
| 7 | 6156 | 1809 | 0 | |
| 8 | 7146 | 2131 | 0 | |
| 9 | 6445 | 2490 | 0 | |
| 10 | 7674 | 3464 | 0 | |
| 11 | 6120 | 3338 | 0 | |
| 12 | 6721 | 3504 | 0 | |
| 13 | 7620 | 2777 | 0 | |
| 14 | 6869 | 3945 | 1453 | |
| 15 | 3799 | 5440 | 330107 | |
| 16 | 6088 | 4071 | 131446 | |
| 17 | 6505 | 3913 | 123897 | |
| 18 | 6465 | 4035 | 195277 | |
| 19 | 7107 | 4392 | 85205 | |
| 20 | 7354 | 4054 | 159896 | |
| 21 | 6593 | 3629 | 4640 | |
| 22 | 7538 | 2957 | 6982 | |

**[0072]** As shown in Table 2, the ASME P92 steels with the symbols 2 and 6 are longer in creep rupture time and are evidently high in creep strength as compared with the ASME P91 steel with the symbol 1. However, the creep-fatigue lives are almost equal to each other. Thus, the ASME P92 steels do not show any significant improvements in creep--fatigue life.

**[0073]** The steels given the symbols 3 to 5 and containing a minute amount of Cu, Ni or Co are parallel in creep strength to the steel with the symbol 2, but they were found to evidently have a decreased creep-fatigue life.

**[0074]** Using the steels with the symbols 2, 6, 7, 8 and 9, the influences of Mo on the creep rupture strength and creep-fatigue strength were examined. The steels given the symbols 7 and 8 and having a low Mo content are inferior in creep-fatigue strength to the steels with the symbols 2 and 6. The steel given the symbol 9 that has a high Mo content is also inferior in creep-fatigue strength.

**[0075]** The steels given the symbols 10 to 13 and containing a minute amount of La, Ce, Ca or Mg are parallel in creep strength and creep-fatigue strength to the steel with the symbol 2, revealing no improved characteristics.

**[0076]** On the contrary, the steels given the symbols A to M and satisfying the conditions specified herein in accordance with the invention, are parallel in creep rupture time to the steel with the symbol 2 but show marked improvements in creep-fatigue life.

**[0077]** The steel given the symbol 14 and having a Nd content lower than the range specified herein in accordance with the invention, shows an unsatisfactory improvement in creep-fatigue strength. On the other hand, the steel given the symbol 15 that contains an excessive amount of Nd is low in creep strength.

**[0078]** The steels given the symbols 16 to 18 and containing a minute amount of Nd and a minute amount of the austenite-forming element Cu, Ni or Co are parallel in creep strength to the steel with the symbol 2 were found to have a improved creep-fatigue strength to some extent, compared with the steel having the symbol 2. However, they are evidently inferior in creep-fatigue strength compared with the steels given the symbols A to M that have no or little elements of Cu, Ni or Co.

**[0079]** The steels given the symbols 19 and 20 and containing Nd within the range specified herein but containing Mo outside the range specified herein are longer in creep-fatigue life as compared with those containing no Nd. However, they are evidently inferior in creep-fatigue strength when compared with the steels given the symbols A to M that have a Mo content within the range specified herein.

**[0080]** The steels with the symbols 21 and 22 have a chemical composition within the range specified herein but the Nd inclusion distribution density thereof does not fall within the range specified herein. In the case of these steels, Nd was added without sufficient deoxidation. As a result, very coarse Nd oxide grains were formed. The Nd inclusion density therein is markedly low and their creep-fatigue lives are at low levels.

[Industrial Applicability]

**[0081]** The steel of the invention is a heat-resistant steel excellent in long-term creep strength and creep-fatigue strength at high temperatures of 600 to 650°C. This steel produces good effects in the form of steel pipes for exchangers, steel plates for pressure vessels and a material for turbines, which are used in such fields as thermal power generation, nuclear power generation and the chemical industry; it is thus very useful from the industrial viewpoint.

## Claims

1. Ferritic heat-resistant steel which comprises C: 0.01 to 0.13%, Si: 0.15 to 0.50%, Mn: 0.2 to 0.5%, P: not higher than 0.02%, S; not higher than 0.005%, Cr: exceeding 8.0% but lower than 12.0%, Mo: 0.1 to 1.5%, W: 1.0 to 3.0%, V: 0.1 to 0.5%, Nb: 0.02 to 0.10%, sol. Al: not higher than 0.015%, N: 0.005 to 0.070%, Nd: 0.005 to 0.050% and B: 0.002 to 0.015%, optionally further contains one or more elements selected among Ta: not higher than 0.04%, Hf: not higher than 0.04%, Ti: not higher than 0.04%, Ca: not higher than 0.005% and Mg: not higher than 0.005%, with the balance Fe and impurities, wherein the content of Ni is lower than 0.3%, the content of Co is lower than 0.3% and the content of Cu is lower than 0.1%, the total content of rare earth elements, except for Nd, is preferably not higher than 0.04% among the impurities, said steel containing Nd inclusions with a diameter of 0.3 to 1 $\mu$m consisting of Nd oxide and composite inclusions comprising Nd oxide and Nd sulphide at a Nd inclusion density of not lower than 10000 inclusions/mm$^3$.

2. Ferritic heat-resistant steel according to Claim 1, which is **characterized in that** the creep-fatigue life thereof under the CP type strain wave form at 600 deg. C under the conditions of a strain rate of 0.01%/sec on the tensile side, a strain rate of 0.8%/sec on the compressive side and a total strain range of 0.5% is not shorter than 5000 cycles.

## Patentansprüche

1. Ferritischer wärmebeständiger Stahl, welcher C: 0,01 bis 0,13%, Si: 0,15 bis 0,50%, Mn: 0,2 bis 0,5%, P: nicht höher als 0,02%, S nicht höher als 0,005%, Cr: 8,0% übersteigend aber niedriger als 12,0%, Mo: 0,1 bis 1,5%, W: 1,0 bis 3,0%, V: 0,1 bis 0,5%, Nb: 0,02 bis 0,10%, sol. Al: nicht höher als 0,015%, N: 0,005 bis 0,070%, Nd: 0,005 bis 0,050% und B: 0,002 bis 0,015% umfasst, optional ferner eines oder mehrere Elemente enthält, die aus Ta: nicht höher als 0,04%, Hf: nicht höher als 0,04%, Ti: nicht höher als 0,04%, Ca: nicht höher als 0,005% und Mg: nicht höher als 0,005% ausgewählt sind, mit dem Restbetrag Fe und Verunreinigungen, wobei der Gehalt an Ni niedriger als 0,3% ist, der Gehalt an Co niedriger als 0,3% ist und der Gehalt an Cu niedriger als 0,1% ist, der Gesamtgehalt an Seltenerdelementen, mit Ausnahme von Nd, unter den Verunreinigungen ist bevorzugt nicht höher als 0,04%, wobei der Stahl Nd Einschlüsse mit einem Durchmesser von 0,3 bis 1 μm, die aus Nd-Oxid bestehen, und Kompositeinschlüsse, die Nd-Oxid und Nd-Sulfid umfassen, enthält bei einer Nd-Einschlussdichte von nicht niedriger als 10000 Einschlüssen/mm$^3$.

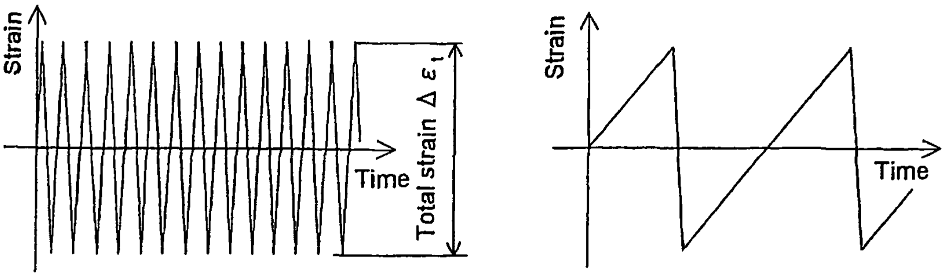
2. Ferritischer wärmebeständiger Stahl nach Anspruch 1, welcher **dadurch gekennzeichnet ist, dass** das Langzeitermüdungsleben davon unter der CP-artigen Belastungswellenform bei 600 Grad C unter den Bedingungen einer Belastungsrate von 0,01%/sec auf der Zugseite, einer Belastungsrate von 0,8%/sec auf der Druckseite und einem Gesamtbelastungsbereich von 0,5% nicht kleiner als 5000 Zyklen ist.

## Revendications

1. Acier ferritique résistant à la chaleur qui comprend : 0,01 à 0,13% de C, 0,15 à 0,50% de Si, 0,2 à 0,5% de Mn, au plus 0,02% de P, au plus 0,005% de S, une quantité supérieure à 8,0% mais inférieure à 12,0% de Cr, 0,1 à 1,5% de Mo, 1, 0 à 3,0% de W, 0, 1 à 0,5% de V, 0,02 à 0,10% de Nb, au plus 0,015% d'Al en solution, 0,005 à 0,070% de N, 0,005 à 0,050% de Nd et 0,002 à 0,015% de B, contient en outre facultativement un ou plusieurs élément(s) choisi(s) parmi : Ta en une quantité d'au plus 0,04%, Hf en une quantité d'au plus 0,04%, Ti en une quantité d'au plus 0,04%, Ca en une quantité d'au plus 0,005% et Mg en une quantité d'au plus 0,005%, le reste étant du Fe et des impuretés, dans lequel la teneur en Ni est inférieure à 0,3%, la teneur en Co est inférieure à 0,3% et la teneur en Cu est inférieure à 0,1%, la teneur totale en éléments de terres rares, à l'exception du Nd, est de préférence d'au plus 0,04% parmi les impuretés, ledit acier contenant des inclusions de Nd avec un diamètre allant de 0,3 à 1 μm constituées de l'oxyde de Nd et des inclusions composites comprenant l'oxyde de Nd et le sulfure de Nd à une densité d'inclusion de Nd d'au moins 10000 inclusions/mm$^3$.

2. Acier ferritique résistant à la chaleur selon la revendication 1, qui est **caractérisé en ce que** la résistance au fluage-à la fatigue de celui-ci sous la forme d'une onde de déformation de type CP à 600°C dans les conditions d'une vitesse de déformation de 0,01%/sec sur le côté de traction, d'une vitesse de déformation de 0,8%/se sur le côté de compression et d'une plage de déformation totale de 0,5% est d'au moins 5000 cycles.

[Fig. 1]



a) PP wave form

b) CP wave form

Fig. 1 Examples of the strain wave form

[Fig. 2]

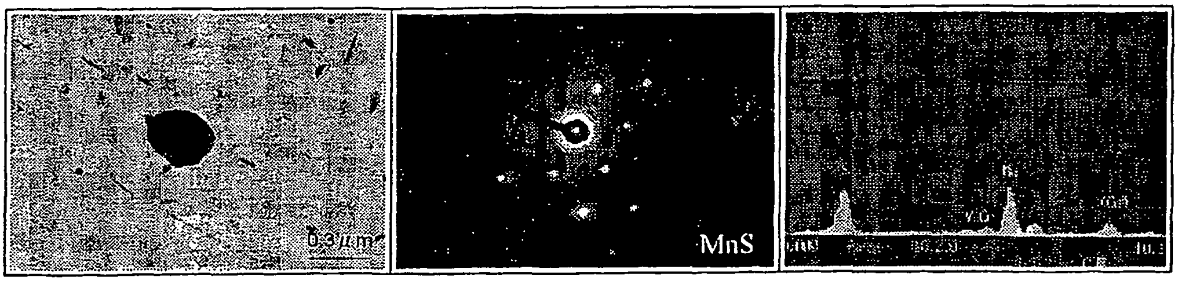


Fig. 2 A sulfide observed in the ASME P92 steel

[Fig. 3]

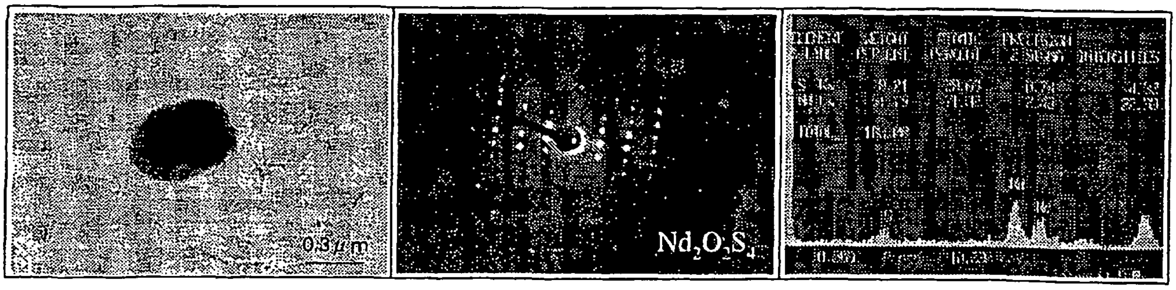


Fig. 3 A "composite inclusion comprising Nd oxide and Nd sulfide" as observed in a Nd-containing steel

## REFERENCES CITED IN THE DESCRIPTION

### Patent documents cited in the description

- JP 2001192781 A **[0007]**
- JP 2002224798 A **[0007]**
- JP 2002235154 A **[0007]**
- JP 2002363709 A **[0008]**