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(54) **High chromium ferritic heat resisting steel and method of heat treatment for the same**

(57) The invention provides a method of heat-treatment for high chromium ferritic heat resisting steel, which comprises the steps of:

(a) heat-treating for 5 seconds or longer high chromium ferritic steel containing chromium (Cr) in amount of 7-12 weight %; one or two elements of molybdenum (Mo) and tungsten (W) as a solid-solution strengthening element; and one or more of elements for forming (a) MX carbonitride(s) at a

temperature higher than both solid-solution temperature of said element(s) for forming the MX carbonitride(s) and a precipitation starting temperature of δ ferrite;

(b) cooling said steel at a rate of 0.5°C/s or faster; and

(c) subsequently tempering said steel.

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Description

[0001] This invention relates to high chromium ferritic heat resisting steel and a method of heat treatment for the same. More particularly, this invention relates to high chromium ferritic heat resisting steel of which both a long-term creep property at high temperatures and toughness at room temperature or lower are improved regardless of compositions, and a method of heat treatment for improving those properties of the high chromium ferritic steel.

[0002] High strength, high toughness, high temperature corrosion resistivity, and oxidation resistivity are required for heat resisting steel which is applied to boilers or high temperature heat resisting and pressure resisting members in nuclear or chemical industry. For example, austenitic stainless steel such as JIS-SUS321H and JIS-SUS347H, low alloy steel such as JIS-STBA24 (2·1/4Cr-1Mo steel) and ferritic steel containing chromium in amount of 9~12 weight % such as JIS-STBA26 have been provided.

[0003] In thermal power plants, temperature and pressure enhancement of steam in the boilers has been particularly considered for the purpose of improving thermal efficiency. For example, instead of an operation under a supercritical condition of 538 °C and 246 bar at present, a ultra supercritical condition of 650 °C and 350 bar is planning.

[0004] Austenitic stainless steel is one of the candidates that meet those conditions. However, since the austenitic stainless steel is expensive, its use in commercial plants is very limited from the economic point of view. In addition, the austenitic stainless steel has a large coefficient of thermal expansion and therefore thermal stress increases as temperature changes, for example, with start and stop operations, which leads to deterioration of a heat resisting fatigue property, scale peeling and stress corrosion cracking.

[0005] instead of the austenitic stainless steel with several defects above-mentioned, improvement of properties of high chromium ferritic steel has been developed. This is because that the high chromium ferritic steel is more excellent than low alloy steel in strength and corrosion resistivity and that, compared with the austenitic stainless steel, the high chromium ferritic steel is cheaper, its thermal conductivity is higher, and coefficient of thermal expansion is smaller.

[0006] As a strengthening means for the high chromium ferritic steel, two methods have been well-known. One is solid-solution hardening by element addition, and the other is precipitation hardening by fine precipitates. Both means have been optimized by composition design.

[0007] Many attempts have been mainly directed to improvement of high temperature strength and toughness or creep properties by adding boron, titanium, and hafnium as well as molybdenum and tungsten. The above-mentioned means has proposed, for example, in Japanese Provisional Patent Publication Nos. 97,832/91, 286,246/95, 62,497/95, 85,847/96, 263,196/93, 311,342/93, 311,343/93, 311,344/93, 311,345/93, and 311,346/93.

[0008] In a sense, it might be natural under the circumstances that property improvement of steel by a structure control resulting from heat treatment has not been studied. However, optimization of precipitation hardening by carbonitrides, i.e., MX, which is very effective for improving creep strength, allows remarkable increase of creep strength.

[0009] The MX carbonitrides include single carbides and nitrides such as VC, NbC, VN and NbN, and composite carbonitrides such as V (C,N) and Nb (C,N). Complete solid-solution to a matrix takes place for each of the single carbides by heating at around 1,100 °C, but, complete solid-solution at 1,100 °C does not occur for any of the single nitrides and composite carbonitrides. Further, solid-solution temperature of the MX carbonitrides is elevated in steel in which at least one of the elements such as boron, titanium and hafnium are doped. For example, solid-solution temperature is increased by 1,200 °C or higher in the case of the steel to which titanium or hafnium is added.

[0010] The increase of solid-solution temperature results in insufficient solid-solution of the MX carbonitrides by normalizing at 1,100 °C or lower and suppression of precipitation of fine MX carbonitrides during subsequent tempering. In addition, it brings about not uniform distribution of fine MX carbonitrides in steel. All of them are causes of decrease of the improvement effect of creep strength by the MX carbonitride.

[0011] In the case that normalizing temperature is higher, solid-solution of the MX carbonitride makes sufficient progress, but at the same time, formation of coarse grains and a δ ferritic phase is promoted. In the steel containing a large amount of W (tungsten), a large amount of the δ ferritic phase is produced in steel because W is one of the elements that forms ferrite. Since the coarse grains and the δ ferrite extremely deteriorate toughness, higher normalizing temperature is not useful means.

[0012] Thus, sufficient solid-solution of the MX carbonitrides brings about formation of coarse grains and the δ ferrite, which deteriorates toughness of steel. Suppression of coarse grains and the δ ferrite causes insufficient solid-solution of the MX carbonitrides, vice versa. Conventional normalizing cannot realize solid-solution of the MX carbonitride together with suppression of the causes of toughness deterioration.

[0013] Now, this invention will become more apparent upon a reading of the following detailed specification and drawings, in which:

Fig. 1 shows microscopic photos showing results of observation of initial structures of Ti-added steel and their structures after heat treatment;

Fig. 2 shows microscopic photos showing results of observation of initial structures of as forging specimens and

their structures after heat treatment;

Fig. 3 shows microscopic photos showing results of observation of initial structures of two-step heat-treated specimens and their structures after heat treatment;

Fig. 4 shows microscopic photos showing results of observation of structures of Ti-added steel when a cooling rate is changed after heat treatment;

Fig. 5 shows microscopic photos showing results of TEM observation of Ti-added steel treated by a conventional manner and a method of this invention; and

Fig. 6 shows microscopic photos showing results of observation of Ti-added steel which is made when a re-austenitizing condition is changed.

[0014] Firstly, this invention provides a method of heat treatment for high chromium ferritic heat resisting steel, which comprises the steps of heat-treating high chromium ferritic steel containing chromium (Cr) in amount of 7~12 weight %, one or two elements of molybdenum (Mo) and tungsten (W) as a solid-solution strengthening element, and one or more of elements for forming a MX carbonitride (s) at a temperature higher than both solid-solution temperature of said element(s) for forming the MX carbonitride(s) and a precipitation starting temperature of δ ferrite for 5 seconds or longer, cooling said steel at a rate of 0.5 °C/s or faster, and subsequently tempering the steel.

[0015] Secondly, this invention provides a modification of the above-mentioned method in which a temperature of the steel before heat-treating is preserved at a temperature range of an austenitic single-phase region for homogenization of an initial structure. Thirdly, this invention provides another modification of the above-mentioned method in which a temperature of the steel is preserved at a temperature range of an austenitic single-phase region during cooling. Fourthly, this invention provides further another modification of the above-mentioned method in which the steel is heat-treated for 30 seconds or longer.

[0016] Fifthly, this invention provides high Cr ferritic heat resisting steel heat-treated according to the above-mentioned method.

[0017] In the method of heat treatment of high Cr ferritic heat resisting steel of this invention, high Cr ferritic steel containing Cr in amount of 7~12 weight %, one or two elements of Mo and W as a solid-solution strengthening element, and one or more of elements for forming a MX carbonitride(s) is heat-treated at a temperature higher than both solid-solution temperature of said element (s) for forming the MX carbonitride(s) and a precipitation starting temperature of δ ferrite for 5 seconds or longer, cooling said steel at a rate of 0.5 °C/s or faster, and subsequently tempering the steel.

[0018] As far as precipitation hardening of the MX carbonitride is possible, any composition of high Cr ferritic steel is objective for this invention. Conventional steel maybe used. In general, a composition with the ratio of ingredients is exemplified for the high Cr ferritic steel.

[0019] The MX carbonitride is expressed MC, i.e., metal element combines with carbon at a ratio of 1:1, among carbides formed when an alloy element M is added to a Fe-C steel. When nitrogen (N) is contained in steel, the MX carbonitride is expressed M(C,N). The element for forming the MX type carbonitride is an alloy element(s) M, which is added to steel. Typically, the element M can be selected from elements that belong to the III, IV, and V groups in the periodic table. For example, vanadium (V), niobium (Nb), tantalum (Ta), hafnium (Hf), titanium (Ti), and zirconium (Zr) are preferably selected for the M.

[0020] The high Cr ferritic steel with such a composition is given to a shape by casting or hot working.

[0021] Casting or hot working is well-known as a means for giving steel a shape and its purpose is to facilitate heat treatment at high temperatures. The manner is not restricted to any special one. Various kinds of manners such melting and hot forging as have generally performed can be adopted.

[0022] In this invention, the heat treatment is performed at a temperature higher than both solid-solution temperature of the above-mentioned element(s) for forming the MX carbonitride(s) and a precipitation starting temperature of δ ferrite for 5 seconds or longer. With respect to a heating rate of the heat treatment, rapid heating, for example, around 10°C/s, is preferable because it can prevent from recrystallization of coarse austenite and formation of δ ferrite. For example, high-frequency induction heating can be used. The existing high-frequency induction heating system for local heating can be also applied to the heat treatment in this invention because an allowable range of cooling rate in the subsequent cooling step is relatively wide.

[0023] Complete solid-solution of the MX carbonitride to a matrix of the high chromium ferritic steel is indispensable for tempering as a post-step, which can uniformly and finely precipitate the MX carbonitride in the matrix. This is one of the keys of this invention. In this meaning, it is reasonable that the temperature of the heat treatment is one that can carry out perfect solid-solution of the MX carbonitride. For example, the temperature can be at least 20 °C higher than solid-solution temperature of the MX carbonitride. 30 °C higher than the solid-solution temperature is more preferable.

[0024] Precipitation of δ ferrite is also important in the heat treatment of this invention. The heat treatment at a higher temperature than the δ ferrite precipitation starting temperature causes δ ferrite phases to precipitate at triple point of austenitic grain boundaries. The precipitated δ ferritic phases are possible to suppress grain growth of austenite. As the conventional heat treatment has been carried out only at a temperature range of an austenite single-phase region,

there is no brake on austenite grain growth and austenite grains easily become coarse, resulting in decrease of toughness of high Cr ferritic steel. In the heat treatment of this invention, coarse grains are suppressed by precipitating the δ ferritic phases, which have been thought to be one of the causes of toughness decrease, at triple point of austenitic grain boundaries. The temperature of the heat treatment is, therefore, higher than δ ferrite precipitation starting temperature.

[0025] In this invention, the heat treatment is carried out at a higher temperature between solid-solution temperature of the element(s) for forming the MX carbonitride and δ ferrite precipitation starting temperature. However, it should be taken into account that improper treatment at an excessively higher temperature induces coarser grains and excessive formation of ferrite.

[0026] Designing heat treatment time can suppress coarser grains and excessive formation of δ ferrite and realize sufficient solid-solution of the MX carbonitride.

[0027] Namely, when heat treatment time at a higher temperature is within a minute, solid-solution of the MX carbonitride can be promoted. At an optimal treatment temperature, time which is required for almost perfect solid-solution of the MX carbonitride can be possibly longer than about 5 seconds. For the solid-solution of even fine MX carbonitrides to a matrix, 30 second or longer is more preferable.

[0028] After heat treatment, the high Cr ferritic steel is cooled. With respect to cooling, it may be concerned that the solid-solved MX carbonitride would be precipitated and that a slight amount of the δ ferritic phases formed during heat treatment at a much higher temperature than δ ferrite precipitation starting temperature would become coarse.

[0029] If a cooling rate is slow such as 0.1 °C/s, a large amount of the MX carbonitride precipitates between interfaces of δ ferrite/austenite and the precipitation also occurs in martensite grains which are transformed from austenite. However, when a cooling rate is 0.5 °C/s or faster, only a slight amount of the MX carbonitride precipitates in the δ ferritic phases formed during the heat treatment or between the interfaces of δ ferrite/austenite. In the case that a cooling rate is 1 °C/s or slower, an amount of δ ferritic phase sometimes increases as the cooling rate decreases, but when a cooling rate is 5 °C/s or faster, difference on an amount of δ ferritic phase disappears. Consequently, a cooling rate can be 0.5 /s or faster and approximately 5 °C/s is more preferable.

[0030] Subsequently, the high Cr ferritic steel is tempered. The condition of tempering is not specified and is appropriately devised so as to meet tensile strength that is required at room temperature.

[0031] As described in detail, this invention provides a method of heat treatment for high Cr ferritic heat resisting steel, which allows compatibility of solid-solution of the MX carbonitride with suppression of causes of toughness deterioration and improves both a long-time creep property at high temperatures and toughness at room temperature or lower.

[0032] In the above-mentioned method of heat treatment for high Cr ferritic heat resistant steel, it is under consideration that a temperature of the steel before the above-mentioned heat treatment is preserved at a temperature range an austenitic single-phase region for homogenization of an initial structure.

[0033] Homogenization of an initial structure changes the initial structure into a complete martensitic structure not including δ ferritic phase, and eliminates micro segregation.

[0034] Formation of δ ferrite in high Cr ferritic heat resisting steel is often affected by an initial structure of the steel before heat-treating. If δ ferritic phases exist in an initial structure of steel, δ ferrite easily grows from nuclear δ ferritic phases during the above-mentioned heat treatment. Therefore, even if the above-mentioned heat treatment is carried out at the same conditions, a volume percentage of δ ferritic phase in a final structure is different, i.e., the volume percentage is extremely larger in the case of existing δ ferritic phases in an initial structure than in the case of complete martensitic structure. This suggests us that a complete martensitic initial structure would be effective for suppressing formation of δ ferritic phase. Existence of micro segregation is given to a portion in steel where δ ferrite is easily formed. Consequently, elimination of the micro segregation is also effective.

[0035] Homogenization is, for example, carried out by preserving high Cr ferritic heat resisting steel at a temperature range of an austenitic single-phase region and subsequently cooling in air. Preserving time can be adjusted based on a situation of δ ferritic phase formation in an initial structure, for example. Any appropriate condition for homogenization will be devised.

[0036] Homogenization can make an initial structure of high Cr ferritic heat resisting steel before the above-mentioned heat treatment a complete martensitic structure, which is effective for decreasing δ ferritic phases during heat-treating.

[0037] Further, in this invention, it is also effective that high Cr ferritic heat resisting steel is preserved at a temperature range of an austenitic single-phase region during cooling after heat-treating.

[0038] In the high Cr ferritic heat resisting steel after the above-mentioned heat treatment, δ ferritic phases in amount of a few %~10% are formed. Since, as above-mentioned, a complete martensitic structure is preferable for ensuring more stable toughness, re-austenitizing of residual δ ferritic phases formed during the above-mentioned heat treatment is effective when high Cr ferritic heat resisting steel is applied to use which especially requires toughness.

[0039] Re-austenitizing is achieved by continuously preserving high Cr ferritic heat resisting steel in a temperature range of an austenite single-phase region in the course of cooling after the above-mentioned heat treatment. Preserving

time can be also adjusted according to existence of residual δ ferritic phases. Any appropriate condition for homogenization will be devised.

[0040] On the other hand, when reaustenitizing is subsequently carried out after cooling to nearly room temperature, a final structure is apt to become a duplex grain structure because two different structure changes simultaneously take place, i.e., reverse transformation from martensite to austenite and transformation from ferrite into austenite. From this point of view, reaustenitizing is preferably carried out in the course of cooling as above-mentioned.

[0041] This prevents a final structure from becoming a duplex grain structure, which is possible to obtain high Cr ferritic heat resisting steel with an ordered grain complete martensite structure.

[0042] High Cr ferritic heat resisting steel obtained by the method with several manners above-mentioned has a martensite single-phase structure with uniform grain size and is excellent in long-time creep strength at high temperatures and toughness at room temperature or lower. Therefore, the obtained steel can be applied to materials for boilers or apparatus materials used under high temperatures and high pressures, for example, materials for nuclear power plants and chemical industry apparatuses. More specifically, the obtained steel is applied to steel pipes for heat exchanging, steel plates for pressure vessels and materials for turbines such as disks.

[0043] Now, several examples of this invention will be exemplified along accompanying drawings and this invention will be explained in more detail.

(Example 1)

[0044] The steel with weight of 10 kg, whose composition was 0.15C-0.5Mn-0.3Si-9Cr-3.3W-0.2V-0.05Nb-0.05Ti, was melted, and hot forging and rolling at 1200°C was carried out to make as roll specimen A with a shape of 6 mm square.

[0045] The as roll specimen was heated at 1,050 °C for an hour and subsequently cooled in water to make a specimen B. The adopted operation is conventional normalizing.

[0046] In addition, the as roll specimen was preserved at 1,050 °C for 10 minutes and subsequently heated by high-frequency induction heating to heat treatment temperatures as temperature was increased at the rate of 50 °C/s. The heat treatment temperatures were kept for 5 seconds and then rapid cooling with helium (He) gas was carried out. The heat treatment temperatures were 1,200 °C, 1250 °C, 1300 °C, 1350 °C, respectively. The resultant specimens were named specimen C ~specimen F.

[0047] The initial structure of specimen A, which was not subjected to heat treatment, and the structures of specimens B~F after the heat treatment were observed. MX carbonitrides and ferritic phases are shown in Fig. 1.

[0048] As is similar case in specimen A, many of coarse MX carbonitrides, which were not solid-solved, are observed in specimen B according the conventional manner. Residual MX carbonitrides are observed in specimen C heat-treated at 1,200°C. On the contrary, MX carbonitrides are almost completely solid-solved in specimens D~F. In the Ti-added steel with the above-mentioned composition, solid-solution temperature of MX carbonitrides is about 1,200 °C and δ ferrite precipitation starting temperature when heating was carried out at the rate of 50 °C/s is about 1,130 °C. From these facts, it is confirmed that solid-solution of MX carbonitrides can be sufficiently promoted by the heat treatment according to this invention.

(Example 2)

[0049] The as roll specimen of Example 1 was subjected to the conventional normalizing. That is, the specimen was heated at 1,100 °C for an hour and subsequently cooling in air. After the normalizing, tempering in which the specimen was heated at 780 °C for an hour and subsequently cooling in air was carried out to make specimen G.

[0050] The above-mentioned as roll specimen was heated at 1,300 °C for an hour, subsequently rapid-cooling with He gas according to this invention. The resultant specimen was subjected to tempering in which the specimen was heated at 780 °C for an hour and subsequently cooling in air to make specimen H.

[0051] Table 1 shows the results of a creep test of specimens G and H.

Table 1

Creep rupture time (h)		
Test conditions	660°C, 110Mpa	700°C, 80Mpa
Specimen G	4280	1088
Specimen H	8653	2350

[0052] It is confirmed that application of this invention to steel improves creep strength.

(Example 3)

[0053] The steel with weight of 7 kg, whose composition was 0.14C-0.5Si-8.5Cr-2W-0.2V-0.05Nb-0.05Ti, was melted, and hot forging at 1200°C was carried out to make as forging specimen a1.

[0054] The as forging specimen was subjected to homogenization by preserving the specimen at 1,050 °C for 24 hours. After homogenization, the specimen was preserved at 1,100 °C for an hour and subsequently cooled in air in order to adjust grain size to be approximately 50 μm. The resultant specimen a2 was a two-step heat-treated specimen.

[0055] The as forging specimen (specimen a1) was subjected to the conventional normalizing, in which the specimen was heated at 1,100 °C for an hour and subsequently cooled in water, to make specimen b1. The resultant specimen was further subjected to heat treatment, in which the specimen was preserved at 1,200 °C, 1,250 °C, 1,300 °C, and 1,350 °C for 5 seconds, respectively, to make specimens c1~f1.

[0056] The two-step heat-treated specimen (specimen a2) was subjected to such conventional treatment to make specimen b2 and was further preserved at the above-mentioned temperatures for 5 seconds to make specimens c2~f2.

[0057] An elevation rate of temperature was 50 °C/s in each heat treatment.

[0058] The results of structure observation of specimens a1 ~f1 are shown in Fig. 2 and the results of structure observation of specimens a2~f2 are shown in Fig. 3.

[0059] As shown in Figs. 2 and 3, while δ ferrite is formed in an initial structure of the as forging specimen (specimen a1), δ ferrite is not formed in an initial structure of the two-step heat-treated specimen (specimen a2).

[0060] In both of the specimens b1 and b2, many of coarse MX carbonitrides, which are not solid-solved, are observed. On the contrary, MX carbonitrides existing in the initial structure (specimens a1 and a2) are completely solid-solved in specimens d1~f1 and specimens d2~f2.

[0061] In the Ti-added steel with the above-mentioned composition, solid-solution temperature of MX carbonitrides is about 1,220 °C and δ ferrite precipitation starting temperature when heating was carried out at the rate of 50 °C/s is about 1,240 °C. From these facts, it is confirmed that solid-solution of MX carbonitrides can be sufficiently promoted by the heat treatment according to this invention.

[0062] The situation of δ ferrite formation in the Ti-added steel is much different between the as forging specimen and the two-step heat-treated specimen.

[0063] With respect to the as forging specimen (specimen a1), coarse δ ferrite is observed in specimens c1~f1 even if they were heat-treated.

[0064] With respect to the two-step heat-treated specimen (specimen a2), δ ferrite is not observed in specimens c2 and d2 that were heat-treated at 1,250 °C or lower. But a slight amount of δ ferrite is observed at a triple point of grain boundaries in specimens e2 and f2 that were heat-treated at 1,300 °C or higher.

[0065] From these results, it is understood that sufficient homogenization at an austenitic single-phase region before heat treatment to change an initial structure into a complete martensitic structure is effective for suppression of δ ferrite formation.

[0066] In spite that specimen e2 was heat-treated at 1,300 °C, coarse grains are not formed in comparison with specimen a2. This suggests us that when δ ferrite precipitation temperature is higher than solid-solution temperature of MX carbonitrides, heat-treating at a higher temperature than δ ferrite precipitation temperature would be effective for suppressing coarse grains.

(Example 4)

[0067] From the detailed observation of the structure of specimen e2, fine MX carbonitrides exist in a martensitic matrix.

[0068] It is also confirmed that the fine MX carbonitrides are almost completely solid-solved when preserving time at 1,300 °C is 30 seconds or longer.

[0069] In the case that preserving time is 60 seconds or longer, a dominant area of δ ferrite is only a few % and therefore the steel has feasibility to be applied to boiler tubes which do not strictly require toughness.

(Example 5)

[0070] The Ti-added steel with the same composition as in Example 3 was preserved at 1,300°C for 60 seconds and subsequently cooled. The cooling rate was changed in seven-grade from rapid cooling of 200 °C/s with He gas to slow cooling of 0.1 °C/s. The results of structure observation are shown in Fig. 4.

[0071] As shown in Fig. 4, in the Ti-added steel cooled at the rate of 0.1 °C/s, a large amount of MX carbonitrides is precipitated near interfaces between δ ferrite/austenite. In the Ti-added steel cooled at the rate of 0.5 °C/s or faster, MX carbonitrides are not precipitated in a martensitic matrix, although a few MX carbonitrides are precipitated in δ ferritic phases.

[0072] From the viewpoint of solid-solution of MX carbonitrides, a cooling rate after preserving at temperatures is required to be 0.5 °C/s or faster.

[0073] On the other hand, the amount of δ ferritic phases is not different remarkably, but the amount of δ ferritic phases extremely increases when a cooling rate is 1 °C/s or slower.

[0074] Consequently, it is understood that a cooling rate of 5 °C/s or faster is preferable when reaustenizing after heat treatment is not carried out.

(Example 6)

[0075] The Ti-added steel with the same composition as in example 3 was subjected to the conventional normalizing in which the specimen was heated at 1,050 °C for an hour and subsequently tempering at 760 °C for an hour to make specimen A. According to this invention, the same Ti-added steel was preserving at 1,300 °C for 30 seconds and subsequently cooled at the rate of 5 °C/s. Then, the steel was subjected to tempering at 760 °C for an hour to make specimen B.

[0076] The results of TEM observation of specimens A and B are shown in Fig. 5.

[0077] In specimen A obtained according to the conventional manner, extremely coarse MX carbonitrides exist, but fine MX carbonitrides which greatly contribute to creep strength are little observed.

[0078] On the contrary, in specimen B according to this invention, any of coarse MX carbonitrides does not exist and a large amount of fine MX carbonitrides is precipitated in a matrix.

[0079] It is reasonably concluded that the method of heat treatment of this invention can improve creep strength of high Cr ferritic heat resisting steel.

(Example 7)

[0080] When high Cr ferritic heat resisting steel is used for thick parts such as main steam pipes for boilers, high toughness is particularly required. In this case, it is preferable that no δ ferritic phase is contained in the high Cr ferritic heat resisting steel. A slight amount of δ ferritic phases that are formed by heat treatment will be dangerous.

[0081] The same two-step heat-treated specimen as in Example 3 was preserved at 1,300 °C for 60 seconds and subsequently cooled to room temperature at the rate of 5 °C/s. Then, the specimen was again heated at 1,100 °C for reaustenizing to make a reheated material A.

[0082] Similarly, the two-step heat-treated specimen was preserved at 1,300 °C for 60 seconds and subsequently cooled to 1,100 °C at the rate of 5 °C/s. Then, the specimen was preserved at 1,100 °C for 5 seconds and rapidly cooled for reaustenizing to make continuously heat-treated material B.

[0083] The results of structure observation of these reheated and continuously heat-treated materials are shown in Fig. 6.

[0084] The reheated material A, of which grain sizes varies largely, has duplex grain structure. On the contrary, continuously heat-treated material B, of which grain sizes rarely varies, and has a remarkably good and ordered structure.

[0085] From these facts, it is understood that effective reaustenizing after heat treatment is continuously performed without cooling to room temperature.

[0086] Furthermore, since steel with an ordered martensitic structure is obtained according to this invention, a series of homogenization before heat treatment and continuously reaustenizing after heat treatment are very effective when making steel which is required high toughness.

[0087] It is needless to mention that this invention is not limited to the above-mentioned examples and that various modifications with respect to details are possible.

Claims

1. A method of heat-treatment for high chromium ferritic heat resisting steel, which comprises the steps of:

(a) heat-treating for 5 seconds or longer high chromium ferritic steel containing chromium (Cr) in amount of 7-12 weight %; one or two elements of molybdenum (Mo) and tungsten (W) as a solid-solution strengthening element; and one or more of elements for forming (a) MX carbonitride(s) at a temperature higher than both solid-solution temperature of said element(s) for forming the MX carbonitride(s) and a precipitation starting temperature of δ ferrite;

(b) cooling said steel at a rate of 0.5 °C/s or faster; and

(c) subsequently tempering said steel.

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2. A method as claimed in claim 1 wherein at least one of said elements is added to steel whereby to form a MX carbonitride expressed as MC, i.e. wherein said element combines with carbon at a ratio of 1:1.
- 5 3. A method as claimed in claim 1 wherein at least one of said elements is added to steel in which nitrogen is contained whereby to form a MX carbonitride expressed as M(C,N).
4. A method as claimed in any one of claims 1 to 3 wherein said element or elements are alloy elements.
- 10 5. A method as claimed in any preceding claim wherein said element or elements M is selected from elements of groups III, IV and V in the periodic table.
6. A method as claimed in claim 5 wherein said element or elements M are selected from vanadium, niobium, tantalum, hafnium, titanium and zirconium.
- 15 7. The method as claimed in any preceding claim, wherein a temperature of the steel before heat-treating is preserved at a temperature range of an austenitic single-phase region for homogenization of an initial structure.
8. The method as claimed in any preceding claim, wherein a temperature of the steel is preserved at a temperature range of an austenitic single-phase region during cooling.
- 20 9. The method as claimed in any preceding claim, wherein the steel is heat-treated for 30 seconds or longer.
10. High Cr ferritic heat resisting steel, which is characterised in that said steel is heat-treated according to the method as claimed in any preceding claim.
- 25 11. Use of the high Cr Ferritic heat resisting steel of claim 10 in the manufacture of boilers or high temperature heat resisting and pressure resisting members in nuclear or chemical industry.

Fig. 1

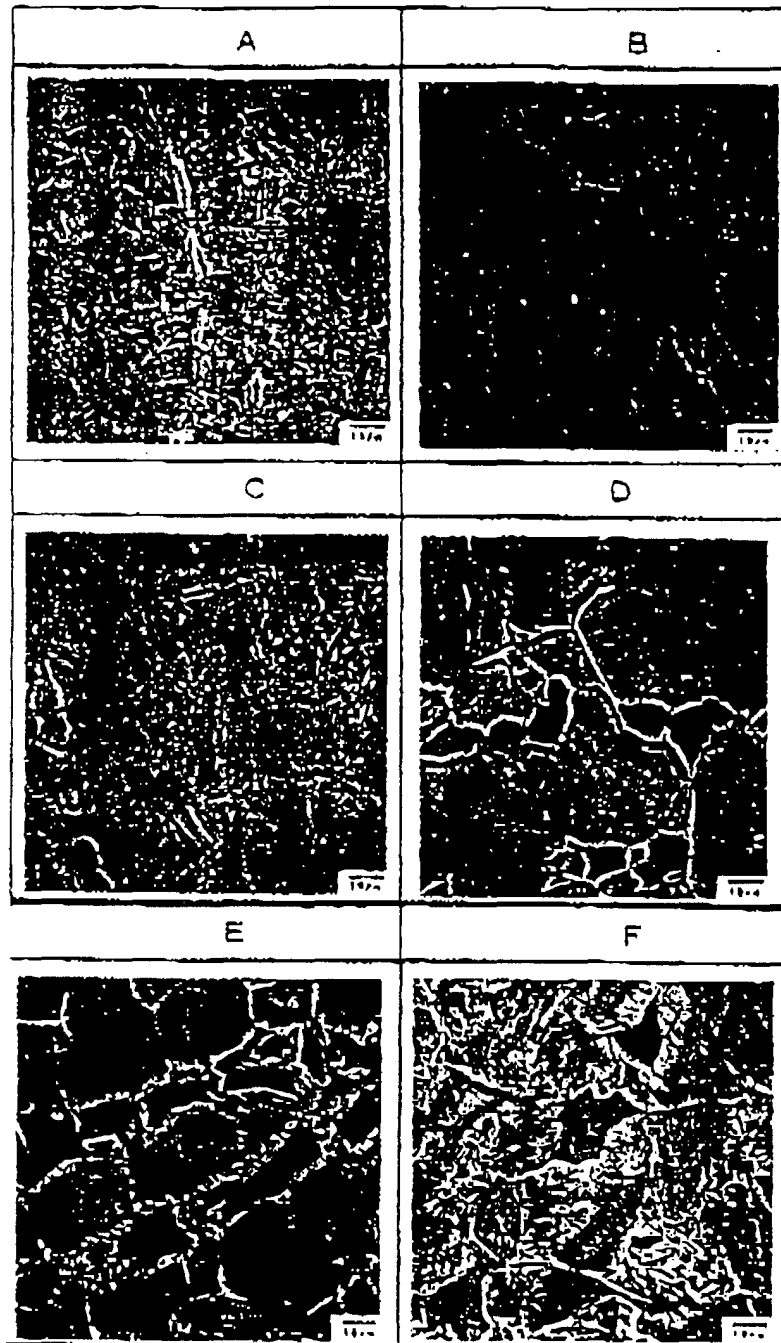


Fig. 2

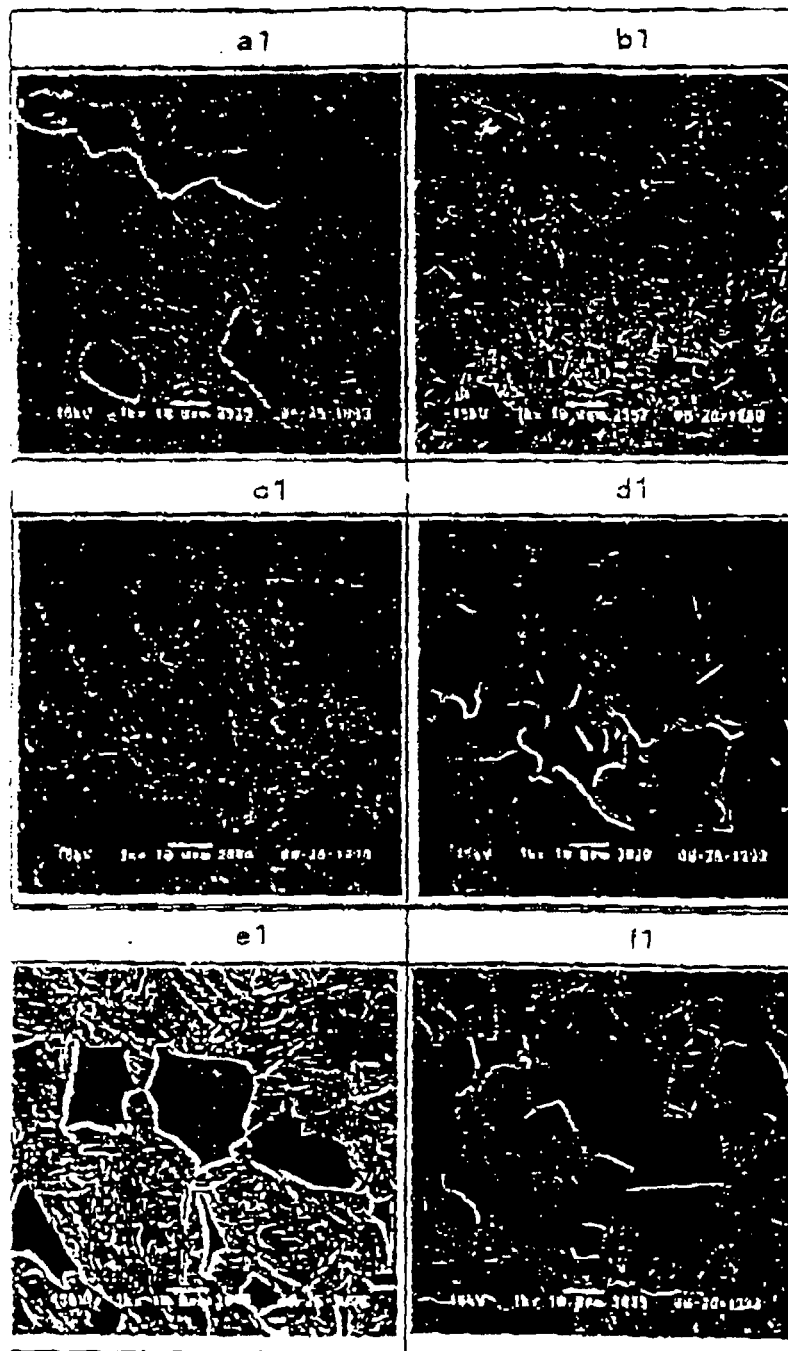


Fig. 3

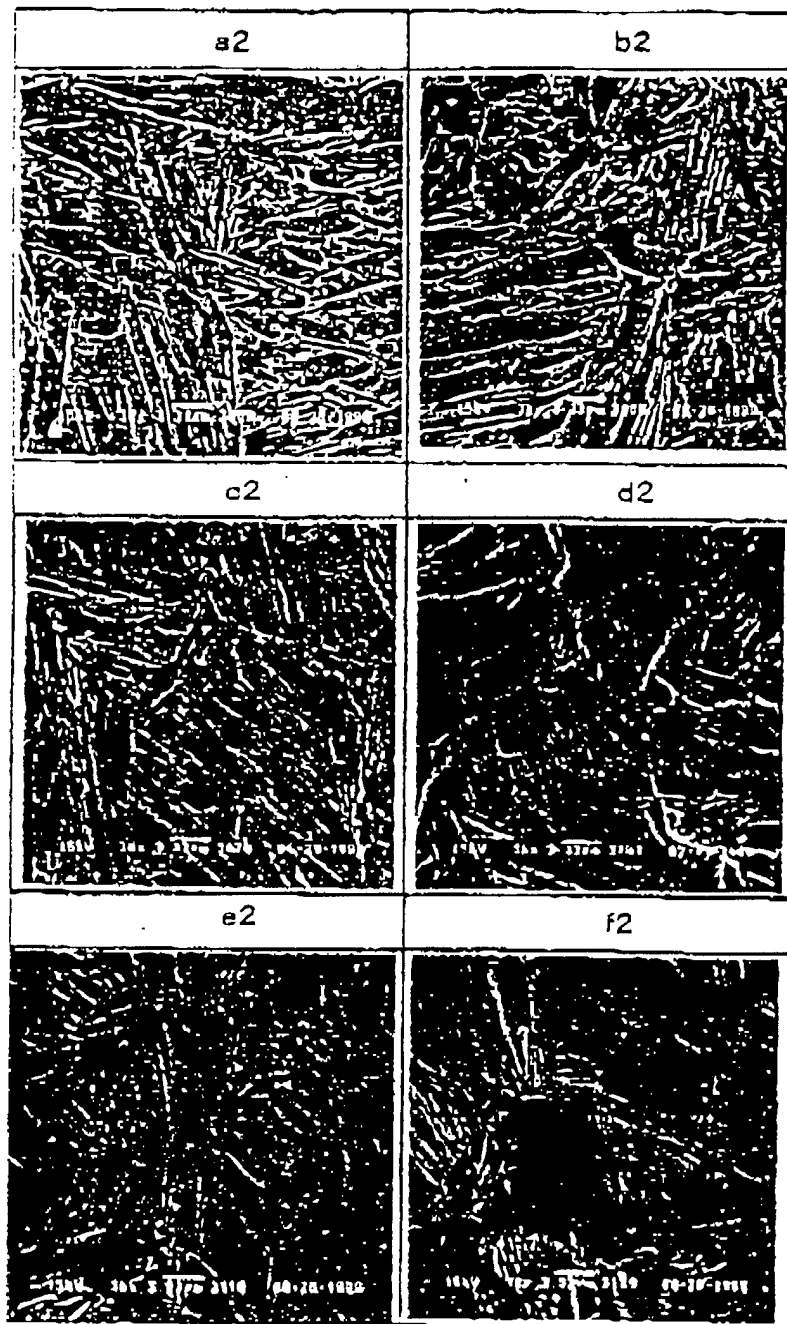


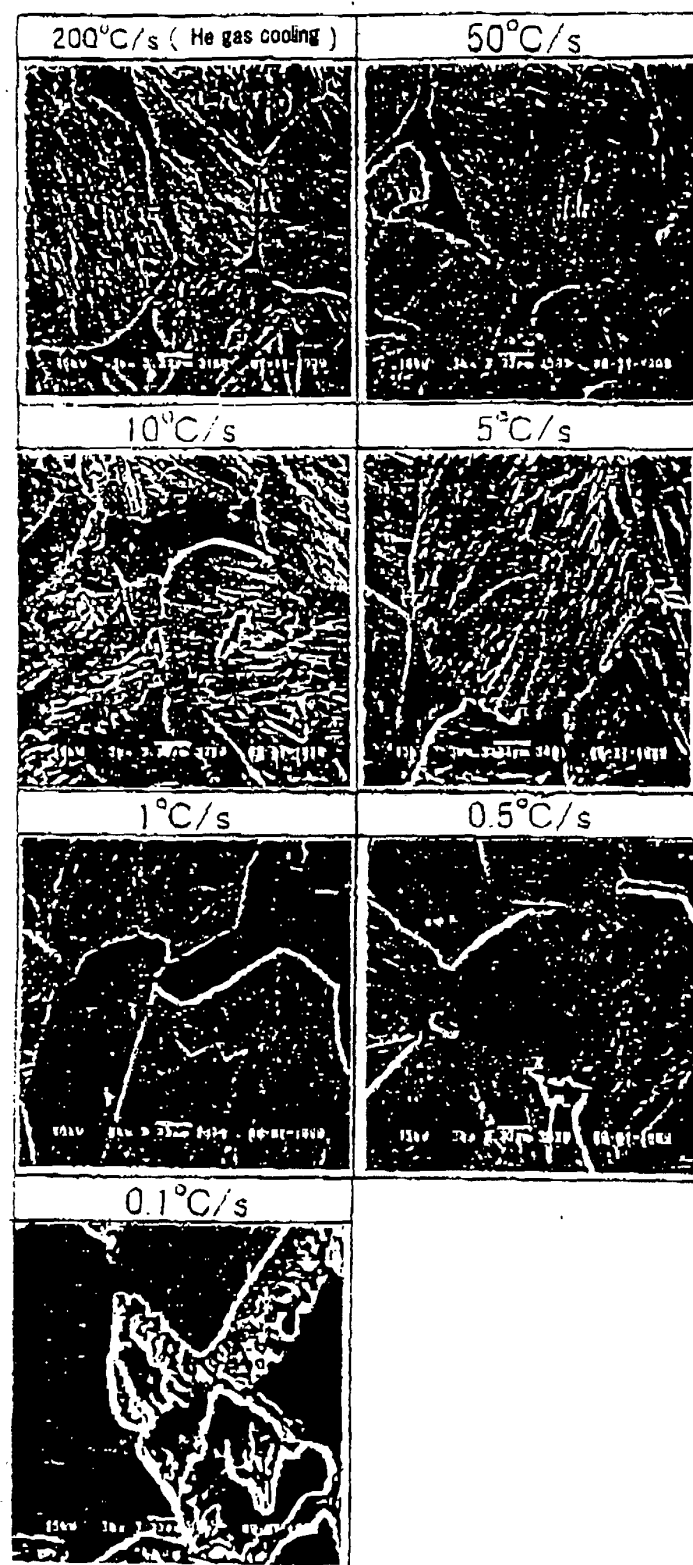
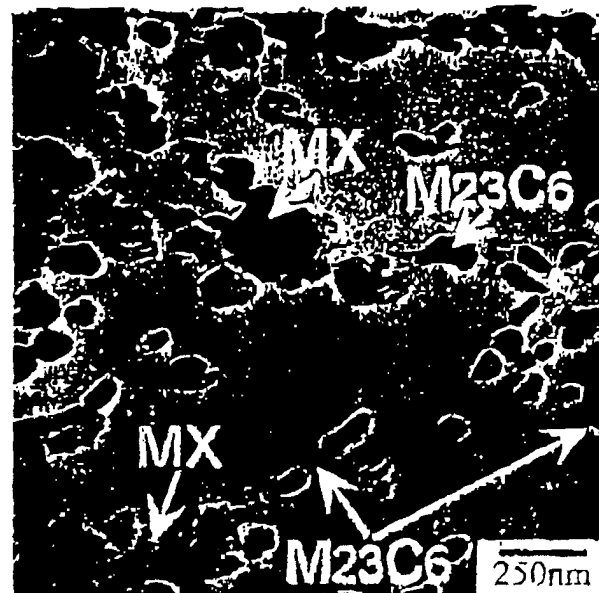
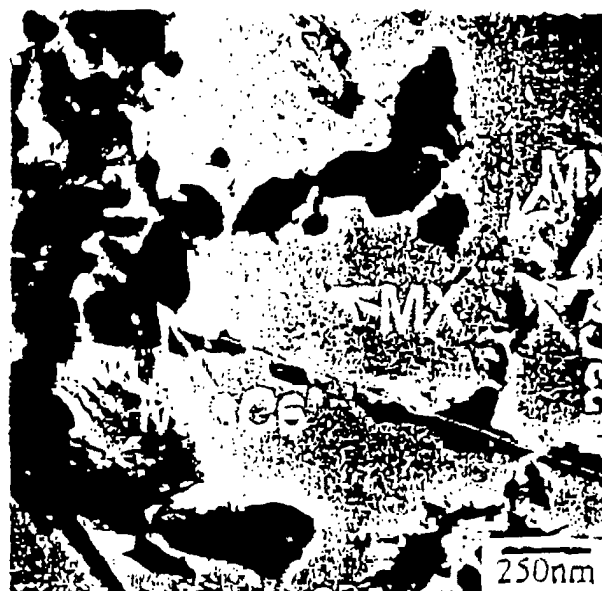
Fig. 4

Fig. 5



A



B

Fig. 6

