



(11) **EP 2 312 006 A1**

(12) **EUROPEAN PATENT APPLICATION**
published in accordance with Art. 153(4) EPC

(43) Date of publication:
20.04.2011 Bulletin 2011/16

(51) Int Cl.:
C22C 38/00 (2006.01) C22C 38/58 (2006.01)
C21D 6/00 (2006.01)

(21) Application number: **09804865.5**

(86) International application number:
PCT/JP2009/062970

(22) Date of filing: **17.07.2009**

(87) International publication number:
WO 2010/016378 (11.02.2010 Gazette 2010/06)

(84) Designated Contracting States:
AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO SE SI SK SM TR
Designated Extension States:
AL BA RS

(72) Inventors:
• **MURAKAMI Yukitaka**
Fukuoka-shi
Fukuoka 819-0395 (JP)
• **MINE Yoji**
Fukuoka-shi
Fukuoka 819-0395 (JP)
• **KANEZAKI Toshihiko**
Fukuoka-shi
Fukuoka 819-0395 (JP)

(30) Priority: **06.08.2008 JP 2008202713**

(74) Representative: **Steinmeister, Helmut**
Patentanwälte
TER MEER STEINMEISTER & PARTNER GbR
Artur-Ladebeck-Strasse 51
33617 Bielefeld (DE)

(71) Applicant: **National Institute of Advanced Industrial Science and Technology**
Tokyo 100-8921 (JP)

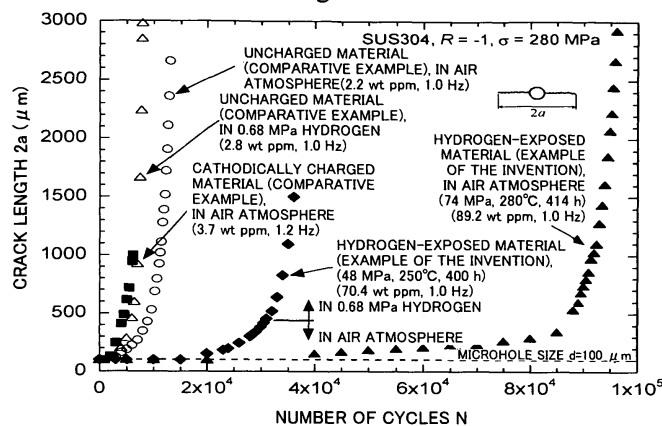
(54) **AUSTENITIC STAINLESS STEEL AND PROCESS FOR HYDROGENATION OF SAME**

(57) Disclosed are an austenitic stainless steel, and a hydrogenation method thereof, in which occurrence of fatigue cracks and growth of fatigue cracks are suppressed by charging the austenitic stainless steel with hydrogen.

strength characteristics of austenitic stainless steel are improved by bringing the amount of diffusible hydrogen and non-diffusible hydrogen contained in the austenitic stainless steel to 0.0030 wt% (30 wt ppm) or higher. The austenitic stainless steel is subjected to a thermal treatment at a heating temperature of 200 to 500°C for up to 460 hours in a hydrogen environment. The hydrogen (H) contained in the austenitic stainless steel is brought thereby to 0.0030 wt% (30 wt ppm) or higher.

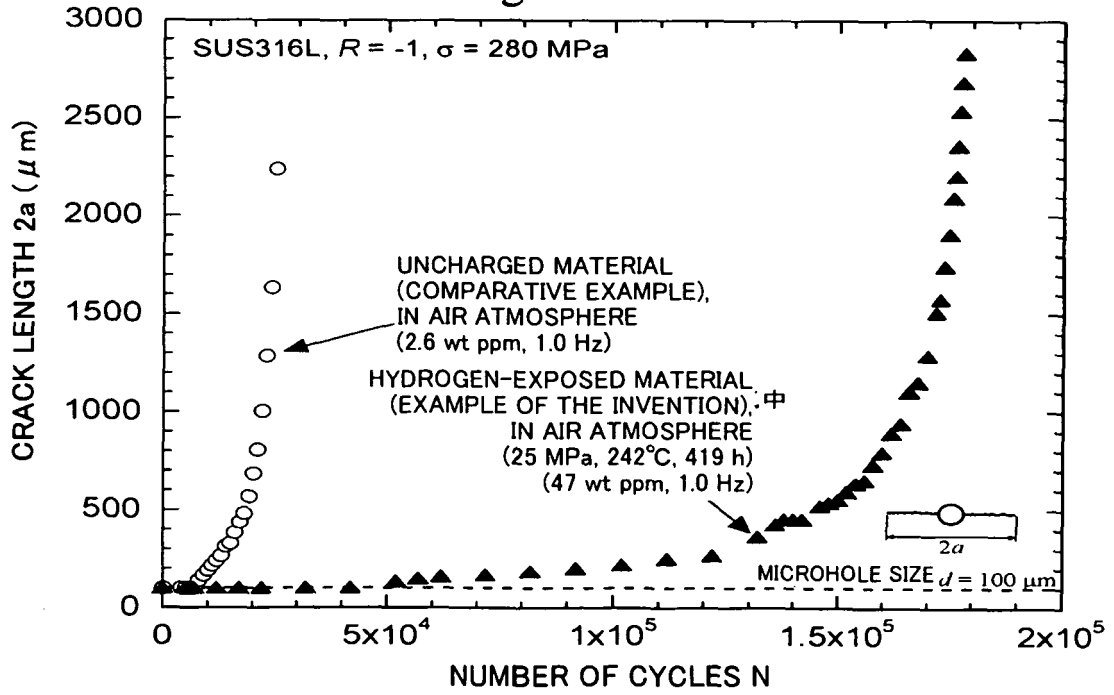
In particular, focusing on the amount of diffusible hydrogen and non-diffusible hydrogen, which cause hydrogen embrittlement in austenitic stainless steel, the fatigue

Fig.6A



EP 2 312 006 A1

Fig.6B



Description

TECHNICAL FIELD

5 **[0001]** The present invention relates to an austenitic stainless steel, and to a hydrogenation method thereof. More particularly, the present invention relates to an austenitic stainless steel having reduced hydrogen embrittlement and exhibiting superior fatigue characteristics, and to a hydrogenation method of such an austenitic stainless steel. In particular, the present invention relates to an austenitic stainless steel in which occurrence of fatigue cracks and growth of fatigue cracks in the austenitic stainless steel can be suppressed by causing 30 wt ppm or more of hydrogen to be stored in the surface of, or throughout, the austenitic stainless steel.

BACKGROUND ART

15 **[0002]** The use of hydrogen as a next-generation energy source has received considerable attention from the standpoint of global environmental concerns. Hence, development and research on this topic are quite active. In particular, the development and practical application of stationary fuel cells, fuel cell-powered vehicles and the like that utilize hydrogen as fuel has become a major target of attention. The use of stainless steel as a material for high-pressure hydrogen tanks and parts thereof, as well as piping and the like in such fuel cell systems, has been explored (for example, Patent document 1).

20 **[0003]** The components of a typical austenitic stainless steel are set forth in Table 1. The first column in Table 1 lists the names of stainless steels and heat-resistant steels as defined in JIS (Japanese Industrial Standards). The last column of Table 1 shows the Vickers hardness of the stainless steel (hereinafter, HV). Other columns correspond to the chemical compositions of the stainless steel, with the units of the components expressed in weight %. The content of hydrogen (H) is expressed as weight ppm at the last component column of Table 1.

25

30

35

40

45

50

55

Table 1

(Component units: wt%, *ppm by weight)												
	C	Si	Mn	P	S	Ni	Cr	Mo	Fe	H*	Other	HV
SUS304 (A)	0.06	0.36	1.09	0.030	0.023	8.19	18.66	-	Balance	2.2	-	176
SUS304 (B)	0.02	0.35	1.02	0.028	0.007	9.06	18.06	-	Balance	1.1	-	-
SUS304 (C)	0.05	0.47	0.99	0.032	0.005	8.14	18.21	-	Balance	2.6	-	-
SUS304 (D)	0.05	0.58	1.24	0.025	0.003	8.09	18.54	-	Balance	2.2	-	176
SUS316 (A)	0.05	0.27	1.31	0.030	0.028	10.15	17.01	2.08	Balance	3.4	-	161
SUS316 (B)	0.05	0.29	1.37	0.030	0.026	10.05	16.89	2.01	Balance	1.2	-	-
SUS316 (C)	0.02	0.53	0.98	0.021	0.001	10.15	16.21	2.08	Balance	1.5	-	164
SUS316L (A)	0.019	0.78	1.40	0.037	0.010	12.08	17.00	2.04	Balance	2.6	-	157
SUS316L (B)	0.010	0.53	0.77	0.023	0.001	12.13	17.16	2.86	Balance	1.5	-	145
SUS310S (A)	0.02	0.34	1.12	0.023	0.001	19.22	24.02	-	Balance	2.8	-	132
SUS310S (B)	0.01	0.34	1.07	0.024	0.001	19.22	24.05	-	Balance	2.4	-	-
SUS310S (C)	0.04	0.42	0.38	0.019	<0.001	20.31	24.69	-	Balance	4.7	-	151
SUH660 (A)	0.04	0.05	0.42	0.016	0.001	24.30	13.59	1.09	Balance	1.2	V = 0.26, Al = 0.17, Ti = 2.22, B = 0.003	-

[0004] As is known, hydrogen penetrates into metallic materials and reduces both the static strength and fatigue strength of the material (for instance, Non-patent documents 1 and 2). Various processes for removing such hydrogen, and methods for predicting the effect of hydrogen, have been proposed. In the method disclosed in Patent document 2, for example, austenitic stainless steel is thermally treated, after a plating process, by being kept at a temperature of 270 to 400°C for 10 minutes or longer, to remove hydrogen thereby, in order to prevent hydrogen embrittlement. Patent document 3 discloses a method wherein the extent of hydrogen embrittlement of austenitic stainless steel is predicted and determined based on the chemical composition thereof.

[0005] Non-patent document 1 discloses fatigue test results for austenitic stainless steels according to SUS304, SUS316, and SUS316L. The fatigue tests are conducted by comparing these austenitic stainless steels charged with hydrogen versus austenitic stainless steels not charged with hydrogen. The results of such a comparison shows that the fatigue crack growth rate of hydrogen-charged SUS304 and SUS316 is faster than in the corresponding uncharged steels. However, no clear difference is seen in the case of SUS316L.

[0006] In addition, Non-patent document 1 discloses fatigue test results for JIS SUS304 and SUS316L austenitic stainless steels after a test piece is prestrained and a microhole of about 100 μm is formed therein. The fatigue crack growth rate is accelerated ten-fold in hydrogen-charged SUS304 compared with an uncharged case. The fatigue crack growth rate is accelerated two-fold in SUS316L.

[0007] However, even meta-stable austenitic stainless steel can undergo mechanically-induced martensitic transformation due to cold-working and cyclic stress. Practitioners in this industry, including groups of researchers in academic societies, have commonly believed that hydrogen has almost no effect on the fatigue crack growth rate in austenitic stainless steels such as JIS SUS316L. Non-patent document 1 discloses results that defy this common belief. This is the more significant in that the results were obtained by applying cyclic loading at a low frequency of 5 Hz or less.

[0008] Specifically, it has been shown that the growth rate of fatigue cracks is accelerated by low-frequency cyclic loading in austenitic stainless steel such as SUS316L. Meanwhile, Non-patent document 2 points out the following: "(3) The martensitic phase resulting from transformation in austenitic stainless steel becomes a pathway for hydrogen diffusion throughout the material, and the diffusion coefficient of hydrogen is increased thereby" (page 130). Non-patent document 3 indicates that growth of fatigue cracks in austenitic stainless steels SUS304 and SUS316L can be suppressed by removing non-diffusible hydrogen in ordinary steelmaking processes.

[0009]

Patent document 1: Japanese Patent Application Laid-open No. 2004-339569

Patent document 2: Japanese Patent Application Laid-open No. H10-199380

Patent document 3: Japanese Patent Application Laid-open No. 2005-9955

Non-patent document 1: Toshihiko KANEZAKI, Chihiro NARAZAKI, Yoji MINE, Saburo MATSUOKA, and Yukitaka MURAKAMI: "The effect of hydrogen on fatigue crack growth of prestrained austenitic stainless steel". The Japan Society of Mechanical Engineers [No. 05-9] Proceedings of the 2005 Annual Meeting of JSME/MMD, M&M 2005 (Nov. 4 to 6, 2005, Fukuoka) P86, pp. 595-596.

Non-patent document 2: Toshihiko KANEZAKI, Chihiro NARAZAKI, Yoji MINE, Saburo MATSUOKA, and Yukitaka MURAKAMI: "Martensitic transformation and effect of hydrogen on fatigue crack growth in stainless steels". Transactions of the Japan Society of Mechanical Engineers A. Vol. 72, No. 723, (November 2006), pp. 123-130 (manuscript received: May 1, 2006).

Non-patent document 3: Yukitaka MURAKAMI, Toshihiko KANEZAKI, Yoji MINE, Saburo MATSUOKA: "Hydrogen Embrittlement Mechanism in Fatigue of Austenitic Stainless Steels", Metallurgical and Materials Transactions A, 39A(2008-6), pp. 1327-1339 (Manuscript received: November 25, 2007; online publication: April 1, 2008)

[0010] At present, however, sufficient analysis is still lacking on how non-diffusible hydrogen, which is present in grains, and diffusible hydrogen, which is charged from the outside, are related to the aforementioned fatigue crack growth rate in austenitic stainless steels. In addition, the relationships according to which diffusible hydrogen and non-diffusible hydrogen exert an influence on changes in the amount of martensitic transformation, on the effect of acceleration of the hydrogen diffusion rate, and on the fatigue crack growth rate in a material, have not been sufficiently elucidated.

[0011] When used in equipment and devices related to hydrogen fuel utilization, moreover, stainless steel is exposed to a variety of environmental influences, depending on the usage environment. When stainless steel is used, for instance, in high-pressure hydrogen containers, piping and the like in a fuel cell-powered vehicle, filling of the foregoing with hydrogen gas and release through consumption of the hydrogen gas are carried out repeatedly. In other words, hydrogen gas loading and release cycles are repeated in the high-pressure hydrogen container, piping and the like for fuel cell-powered vehicles. These repeated cycles are accompanied by changes in temperature in, for instance, the high-pressure hydrogen container or piping for fuel cell-powered vehicles. It is thought that hydrogen intrudes and diffuses thereupon into the material to a degree greater than the equilibrium level at room temperature.

[0012] Low-frequency cyclic loading occurs also due to, for instance, temperature variations in the outside air tem-

perature. Conceivable examples of cyclic loading due to variations in the outside air temperature include, for instance, compression and expansion of the stainless steel itself, as a result of temperature differences between day and night as well as thermal stress resulting from compression and expansion of parts connected to stainless steel components. As for the frequency of the cycle, the temperature difference between day and night can range from only a few degrees to 10°C or more, one cycle being thus 24 hours long. This means that, for instance, high-pressure hydrogen tanks, equipment for supplying fuel for fuel cells and the like in facilities related to fuel-cell powered vehicles have a cycle measured in single day units as noted above, and the hydrogen fill time is accordingly long. In addition, a fuel cell-powered vehicle is dependent on the environment in which it operates, and experiences hence temperature differences of several °C to several tens of °C, and cycles ranging from sub-seconds to several hours.

DISCLOSURE OF THE INVENTION

[0013] The present invention is based on the above technical background, and attains the following objects.

It is an object of the present invention to provide an austenitic stainless steel for suppressing the occurrence of fatigue cracks and growth of fatigue cracks in the austenitic stainless steel, and to provide a hydrogenation method of such an austenitic stainless steel.

[0014] Another object of the present invention is to provide an austenitic stainless steel wherein the formation of fatigue cracks, and/or fatigue crack growth, is slowed down through addition of hydrogen to 30 wt ppm or more, by focusing on the amount of diffusible hydrogen and non-diffusible hydrogen that cause hydrogen embrittlement in austenitic stainless steel, and to provide a hydrogenation method of such an austenitic stainless steel.

It is yet another object of the present invention to provide an austenitic stainless steel in which the fatigue crack growth rate can be slowed down during low-frequency cyclic loading, and to provide a hydrogenation method for such an austenitic stainless steel.

Definition of terms

[0015] The present invention uses the following technical terms in the meanings defined below. Hydrogen charging refers to causing hydrogen to penetrate into a material. Hydrogen charging method refers to a method in which a material is exposed in a high-pressure hydrogen chamber, a method in which cathodic charging is performed, or a method in which the material is immersed in a chemical solution or the like. Fatigue crack growth refers to enlargement of fatigue cracks in a material through the action of cyclic loading. Fatigue cracks are defects or cracks generated in the material during a manufacturing or working process. Cyclic loading refers to cyclic loading acting on holes or the like that are artificially drilled in the material.

[0016] Fatigue crack growth rate refers to the speed with which a fatigue crack grows, specifically the length by which fatigue crack length increases per unit time. Austenitic stainless steel refers to Cr-Ni steel wherein Cr and Ni are added to Fe to produce a stainless steel having an austenitic phase that exhibits increased corrosion resistance in corrosive environments and the like. Table 1 gives a list of such stainless steels. Austenitic phase refers to a phase of iron, at a temperature range of 911 to 1392°C, in 100% pure iron (Fe), having a face-centered cubic lattice structure (hereinafter, FCC structure).

[0017] Fig. 9A illustrates a face-centered cubic lattice. The austenitic phase can also exist at room temperature when alloying elements such as Cr and Ni are added to Fe. A martensitic phase is a structure obtained by quenching steel from a high-temperature stable austenitic phase. The martensitic phase has a body-centered cubic lattice structure (hereinafter, BCC structure). Fig. 9B illustrates a body-centered cubic lattice. The martensitic phase may arise through the action of stress, such as cold-working and the like, on austenitic-phase stainless steel at ordinary temperature.

[0018] The transformation from an austenitic phase having an FCC structure to a martensitic phase having a BCC structure by cold working is referred to as mechanically-induced martensitic transformation. Diffusible hydrogen refers to hydrogen that is present in the material and escapes from the material, over time, at room temperature. Non-diffusible hydrogen refers to hydrogen present in the material and that cannot escape from the material over time, even at temperatures from room temperature to about 200°C.

[0019] The present invention achieves the above objects on the basis of the following means.

The inventors of the present invention found that the fatigue strength characteristics of austenitic stainless steel can be markedly improved if 30 wt ppm or more of diffusible hydrogen and non-diffusible hydrogen are present in the austenitic stainless steel. The present invention relates to an austenitic stainless steel having an austenitic phase the crystalline structure of which is a face-centered cubic lattice structure, and to a hydrogenation method of the austenitic stainless steel.

[0020] The austenitic stainless steel of the present invention is an austenitic stainless steel having an austenitic phase the crystalline structure of which is a face-centered cubic lattice structure, wherein the austenitic stainless steel undergoes a manufacturing process such that a region in which the concentration of hydrogen (H) comprising diffusible hydrogen and non-diffusible hydrogen contained in the austenitic stainless steel is locally 0.0030 wt% (30 wt ppm) or higher has

a thickness of 100 μm or more from the surface of the austenitic stainless steel into the austenitic stainless steel, and wherein occurrence of fatigue cracks in the austenitic stainless steel is delayed, and/or growth of the fatigue cracks is slowed down.

[0021] The austenitic stainless steel hydrogenation method of the present invention is an austenitic stainless steel hydrogenation method of adding hydrogen to an austenitic stainless steel, in order to increase the concentration of hydrogen in an austenitic stainless steel having an austenitic phase the crystalline structure of which is a face-centered cubic lattice structure, the method comprising the step of heating the austenitic stainless steel at a heating temperature of 80°C or higher in a hydrogen environment, to cause thereby a region in which a local concentration of the hydrogen contained in the austenitic stainless steel is 0.0030 wt% (30 wt ppm) or higher to be formed to a thickness of 100 μm or more from the surface of the austenitic stainless steel into the austenitic stainless steel.

[0022] The concentration of the hydrogen (H) in the entirety of the austenitic stainless steel may have a value of 0.0030 wt% (30 wt ppm) or higher. The fatigue strength characteristics of the austenitic stainless steel are markedly enhanced when the concentration of hydrogen (H) contained in the austenitic stainless steel is 0.0030 wt% (30 wt ppm) or higher throughout the austenitic stainless steel. The concentration of hydrogen throughout the austenitic stainless steel will be referred to hereafter as overall concentration.

[0023] The fatigue strength characteristics of the austenitic stainless steel are markedly enhanced when the concentration of hydrogen (H) contained throughout a region having a thickness of at least 100 μm from the surface of an austenitic stainless steel that has a cross-sectional smallest dimension of 200 μm or greater, is 0.0030 wt% (30 wt ppm) or higher. Hereafter, the concentration of hydrogen throughout a region of a predetermined thickness from the surface of austenitic stainless steel will be referred to as local concentration. The cross-sectional smallest dimension denotes the smallest dimension from among height, length and thickness of an austenitic stainless steel material.

[0024] In the case of an austenitic stainless steel round bar material, for instance, the cross-sectional smallest dimension denotes the diameter. In the case of plate-like austenitic stainless steel, the cross-sectional smallest dimension denotes the plate thickness. Preferably, the local concentration or overall concentration of hydrogen (H) contained in the austenitic stainless steel is 0.0050 wt% (50 wt ppm) or higher.

[0025] The Vickers hardness of austenitic stainless steel containing no more than 0.0005 wt% (5 wt ppm) of hydrogen is defined herein as a Vickers hardness of 1. Austenitic stainless steel manufactured in accordance with conventional processes comprises 5 wt ppm or less of hydrogen, as set forth in Table 1. In other words, the above Vickers hardness corresponds to state where hydrogen is unavoidably taken up during a conventional manufacturing processes, i.e. a hydrogen-uncharged state. The Vickers hardness of austenitic stainless steel in a region containing 30 wt ppm or more of hydrogen is 1.05 or higher.

[0026] To add diffusible hydrogen and non-diffusible hydrogen, the austenitic stainless steel may be subjected to a thermal treatment at a heating temperature of 80°C or higher in a hydrogen environment. Heating is effective within a heating temperature range from 200°C to 500°C. The heating temperature may be lower than a sensitization temperature, which is the temperature at which chromium (Cr) carbides in the austenitic stainless steel precipitate by heating. In the thermal treatment, the austenitic stainless steel may be kept at the above-described heating temperature for up to 460 hours in a hydrogen environment.

[0027] Addition of diffusible hydrogen and non-diffusible hydrogen to austenitic stainless steel may rely, for instance, on a method that involves exposure in a high-pressure hydrogen chamber, a cathodic hydrogen charging method, or a method of immersion in a chemical solution. Preferably, the hydrogen environment is a chamber filled with hydrogen gas at 1 MPa or higher.

[0028] The present invention elicits the following effects. Specifically, the present invention allows realizing an austenitic stainless steel where fatigue crack occurrence and fatigue crack growth are slowed down by bringing the concentration of non-diffusible hydrogen and diffusible hydrogen in the austenitic stainless steel to 30 wt ppm or higher, through a thermal treatment of the austenitic stainless steel at a temperature of 80°C or higher in a hydrogen environment.

BRIEF DESCRIPTION OF THE DRAWINGS

[0029]

Fig. 1 illustrates a hydrogen concentration distribution in a 7 mm-diameter round bar material subjected to cathodic hydrogen charging, as a function of depth from the surface;
 Figs. 2A to 2D are diagrams illustrating schematically an evaluation method of hydrogen concentration distribution;
 Figs. 3A to 3C are diagrams illustrating schematically a fatigue test piece, wherein Fig. 3A is a diagram illustrating the shape of a fatigue test piece in Example 1, Fig. 3B is a diagram illustrating the shape of a fatigue test piece in Example 2, and Fig. 3C is a diagram illustrating the shape of an artificial microhole formed in a fatigue test piece;
 Fig. 4 is a diagram illustrating a relevant test area in a fatigue test piece, the shape of a drilled artificial microhole, and fatigue cracks developing at the artificial microhole and propagating therefrom;

Fig. 5 is a photograph of fatigue cracks arising from the artificial microhole after fatigue testing;

Figs. 6A and 6B are a graph illustrating the relationship between number of cycles and the crack length of fatigue cracks as a result of fatigue testing of a fatigue test piece in Example 1, wherein Fig. 6A corresponds to SUS304 and Fig. 6B corresponds to SUS316L;

Figs. 7A and 7B are a graph illustrating the relationship between number of cycles and the crack length of fatigue cracks as a result of fatigue testing of a fatigue test piece in Example 1, wherein Fig. 7A corresponds to SUS304 and Fig. 7B corresponds to SUS316L;

Fig. 8 is a graph illustrating the relationship between test stress amplitude σ and fatigue life N_f at which a fatigue test piece fractures in a SUS304 material having an artificial microhole;

Figs. 9A and 9B are a set of conceptual diagrams illustrating the lattices of the crystalline structures of an austenitic phase and a martensitic phase, wherein Fig. 9A shows a face-centered cubic lattice structure (FCC) of an austenitic phase, and Fig. 9B shows a body-centered cubic lattice structure (BCC) of a martensitic phase;

Fig. 10 is a graph illustrating an anticipated hydrogen concentration distribution in SUS316L, from the surface towards the interior, after 5 years in a hydrogen gas environment at a temperature of 25°C and pressure of 35 MPa or 70 MPa; and

Fig. 11 is a diagram illustrating a Vickers hardness ratio versus hydrogen concentration in austenitic stainless steel.

BEST MODE FOR CARRYING OUT THE INVENTION

[0030] An embodiment of the present invention is explained next on the basis of experimental examples. An explanation is given first on how hydrogen affects the growth rate of fatigue cracks in austenitic stainless steel. After an ordinary thermal treatment (solution thermal treatment), austenitic stainless steels such as SUS304, SUS316, and SUS316L shown in Table 1 contain 1 to 4.7 wt ppm of non-diffusible hydrogen. Upon placing this heat-treated austenitic stainless steel in a hydrogen environment, hydrogen penetrates into the austenitic stainless steel through the surface, and diffuses into the material.

[0031] The material exhibits a hydrogen concentration distribution from the surface towards the interior. Fig. 1 illustrates a measurement example of the measurement of the hydrogen concentration distribution of a material. Herein, 7 mm-diameter, about 30 mm-long round bars of SUS304, SUS316 and SUS316L(A) set forth in Table 1 were subjected to cathodic hydrogen charging. Thereafter, the hydrogen concentration distribution of the round bars was measured, and the results are plotted in the graph of Fig. 1. The ordinate axis of the graph of Fig. 1 represents hydrogen concentration. The hydrogen concentration units are weight ppm. The abscissa axis of the graph of Fig. 1 represents the distance from the surface of the measurement sample. The units of the distance from the surface are μm . Cathodic hydrogen charging was carried out as follows.

[0032] An anode and a cathode were arranged in an aqueous solution of sulfuric acid, and the anode and the cathode were connected to a power source. The liquid temperature of the aqueous solution of sulfuric acid was held at 50°C. The pH of the aqueous solution of sulfuric acid was 3.5. The current density was 27 A/m². A platinum electrode was used in the anode. Round bars of austenitic stainless steel were used as the cathode. Cathodic hydrogen charging was carried out over 672 hours. Once the round bars were charged with hydrogen, the hydrogen concentration distribution of the round bars was measured in accordance with the procedure described below. The dashed line in the Figure represents hydrogen concentration in a round bar not subjected to hydrogen charging.

[0033] Fig. 2A illustrates an austenitic stainless steel round bar subjected to cathodic hydrogen charging, depicted herein before measurement. As illustrated in Fig. 2A, a disc-like sample for measurement, about 0.8 mm thick, was sliced from the austenitic stainless steel round bar having been subjected to cathodic hydrogen charging. The amount of hydrogen comprised in the sample was measured by thermal desorption analysis. Thereafter, the round bars were ground using emery grinding paper. The solid line in Fig. 2B denotes the round bar after emery grinding. The dashed line in Fig. 2B denotes the round bar of Fig. 2A, the surface of which has been removed through emery grinding. As illustrated in Fig. 2B, a further disc-like sample was sliced again out of the round bar. The hydrogen amount in this latter sample was measured.

[0034] The round bar of Fig. 2B was ground again with emery grinding paper. The emery-ground round bar is denoted in Fig. 2C by a solid line. The dashed line of Fig. 2C is the round bar illustrated in Fig. 2B. As illustrated in Fig. 2C, a further disc-like sample was sliced again out of the round bar. The hydrogen amount in this latter sample was measured. The operation of grinding using emery grinding paper, sample slicing and hydrogen amount measurement was thus repeated as described above. Fig. 2B and Fig. 2C illustrate a respective annular portion removed through grinding with emery grinding paper. The annular portion is the portion between the round bar depicted with a solid line and the portion depicted with the dashed line.

[0035] The hydrogen concentration of the annular portion was worked out by dividing the difference between the hydrogen amount of the sample before emery grinding and the hydrogen amount of the emery-ground sample, by the weight of the annular portion. The ground sample volume can be calculated by subtracting the sample volume after

grinding from the sample volume before grinding, as illustrated in Fig. 2D. The weight of the annular portion and the hydrogen concentration in the annular portion can be worked out, accordingly, on the basis of the ground sample volume. The relationship between the local concentration of hydrogen and depth from the surface of a test piece of the round bar can be obtained thus by repeating the above operation.

[0036] The results illustrated in Fig. 1 show that the region at which the hydrogen local concentration is 0.0030% (30 wt ppm) or higher extends from 5 μm to 60 μm from the surface. Thus, the hydrogen concentration of austenitic stainless steel placed in a hydrogen environment exhibits a gradient derived from penetration of hydrogen through the surface, and ensuing diffusion. A gradient such that hydrogen concentration decreases gradually from the surface towards the interior is to be expected, given that the austenitic stainless steel is used in an actual environment of high-pressure hydrogen gas.

[0037] For example, Fig. 10 illustrates the hydrogen concentration distribution predicted for SUS316L on the basis of a hydrogen solid solubility $K_S=4.64$ wt ppm/ $\text{MPa}^{1/2}$, and a diffusion coefficient $D=8.42 \times 10^{-17}$ mm^2/s . In the case, for instance, of SUS316L, the local hydrogen concentration at the surface is about 0.0031 wt% (31 wt ppm) after use over 5 years at 25°C and a hydrogen pressure of 35 MPa. The local hydrogen concentration at the surface is expected to exhibit a gradient such that the local hydrogen concentration decreases gradually from the surface towards the interior, up to about 400 μm from the surface. The region in which the local hydrogen concentration is 30 wt ppm or higher is expected to extend up to about 5 μm from the surface.

[0038] In the case, for instance, of SUS316L, an envisaged use over 5 years at 25°C and a hydrogen pressure of 70 MPa is expected to result in a local hydrogen concentration at the surface of about 0.0049 wt% (49 wt ppm), and in a hydrogen concentration gradient such that the local hydrogen concentration decreases gradually towards the interior up to about 400 μm from the surface. The region in which the local hydrogen concentration is 30 wt ppm or higher is expected to extend up to about 80 μm from the surface.

[0039] According to conventional knowledge, intrusion of hydrogen into the austenitic stainless steel gives rise to hydrogen embrittlement and impairment of fatigue strength characteristics. However, the below-described fatigue tests revealed that fatigue strength characteristics improved noticeably when the amount of hydrogen that intrudes into the austenitic stainless steel is 30 wt ppm or higher. No hydrogen embrittlement due to intrusive hydrogen was observed when the amount of hydrogen was 30 wt ppm or higher. In particular, the inventors of the present invention carried out the following experiments to observe how the content of hydrogen influenced the fatigue crack growth rate. An example of such an experiment is described next.

[Test piece]

[0040] The materials used were the SUS304, SUS316, and SUS316L(A) (hereinafter, simply SUS316L) austenitic stainless steels set forth in Table 1. A solution thermal treatment was performed on SUS304, and SUS316L. The shape of a fatigue test piece made up of these materials is shown in Fig. 3A and Fig. 3B. The surface of the test piece was finished by buffing after grinding with grade 2000 emery grinding paper.

[0041] In order to facilitate observation of fatigue crack growth, an artificial microhole 100 μm in diameter and 100 μm deep was drilled in the radial direction of the fatigue test piece, at the center of the fatigue test piece in the lengthwise direction, as shown in Fig. 3C. The drill bit had a tip angle of 120°. The bottom of the artificial microhole matched the shape (conical shape) of the tip angle of the drill bit. The artificial microhole was drilled in the center of the test area of the fatigue test piece. The test area is a cylindrical portion at the center of the test piece.

[0042] The length of the cylindrical portion of the test area, i.e. the length of the portion having a same outer diameter, is about 20 mm in the fatigue test piece of Fig. 3A, and of about 14 mm in the fatigue test piece of Fig. 3B. Fig. 4 illustrates an outline of the test area and the shape of the drilled artificial microhole. In the case of a hydrogen-charged fatigue test piece, the piece was buffed again, and the artificial microhole was drilled, immediately once hydrogen charging was over.

[X-ray diffraction]

[0043] The amount of martensite in the test area of the fatigue test piece of austenitic stainless steel was measured by X-ray diffraction. X-ray diffraction was performed using a micro X-ray stress measurement apparatus PSPC-RSF/KM by Rigaku Corporation (location: Akishima, Tokyo, Japan). Quantitative analysis was determined on the basis of the integrated intensity ratio of the diffraction peaks of the austenitic phase {220} plane and the martensitic phase {211} plane, using $\text{CrK}\alpha$ radiation. In SUS304, and SUS316L the content of martensite in the test area before fatigue testing was about 3%.

[0044] In SUS304 and SUS316L the content of martensite in the hydrogen-charged test area before fatigue testing was about 3%. The content of martensite was measured in two places before drilling of the artificial microhole. The first measurement region was a circular region 1 mm in diameter centered on the spot at which the artificial microhole was to be drilled. The second measurement region was a region 1 mm in diameter centered on a spot rotated by 180° about

the lengthwise axis, from the spot where the artificial microhole was to be drilled. In other words, the second measurement region was located on the opposite side of the cylindrical portion with respect to the first measurement region.

[Hydrogen charging method]

5 [0045] Hydrogen charging was performed using a cathodic charging method or a high-pressure hydrogen exposure method. In the cathodic hydrogen charging method, the cathodic hydrogen charging conditions included an aqueous sulfuric acid solution at pH=3.5, a platinum anode, and a current density of $i=27 \text{ A/m}^2$. Cathodic hydrogen charging was performed for 672 hours (4 weeks) at a temperature of 50°C (323 K) of the aqueous solution of sulfuric acid. The aqueous solution of sulfuric acid was replaced once a week to minimize changes in the sulfuric acid concentration resulting from evaporation.

10 [0046] In the case of a high-pressure hydrogen exposure method, the fatigue test piece was placed in a high-pressure hydrogen gas environment at a pressure of 10 MPa, 25 MPa, 48 MPa, 74 MPa or 94 MPa, and a temperature of 235°C, 242°C, 250°C or 280°C, to charge thereby the fatigue test piece with hydrogen. The fatigue test piece of Fig. 3A was charged with hydrogen by being kept for 400 hours, 414 hours, 416 hours or 419 hours, while the fatigue test piece of Fig. 3B was charged with hydrogen by being kept for 200 hours, in the high-pressure hydrogen gas environment.

[Fatigue test method]

20 [0047] In the fatigue test there was used a hydraulic servo-controlled tensile and compressive fatigue testing machine "Servopulser EHF-ED30KN" by Shimadzu Corporation (location: Kyoto-shi, Kyoto, Japan), and a servo-controlled tensile and compressive fatigue testing machine "8500" by Instron. The fatigue test was carried out at a cycling frequency of 0.05 to 1.5 Hz, and a stress ratio of $R=-1$. The cycling frequency was adjusted so that the surface temperature of the test area did not exceed 60°C during the fatigue test. Fatigue cracks were observed, and the length of the fatigue cracks was measured in accordance with the replica method or by using a scanning electron microscope S-2500CX, by Hitachi (location: Chiyoda-ku, Tokyo, Japan).

25 [0048] The fatigue cracks were observed by the replica method was performed as follows. An approximately 0.034 mm-thick acetyl cellulose film (hereinafter, replica film) was immersed in methyl acetate liquid for a short time, and was then affixed to the observation site of the fatigue test piece. Once dried, the replica film was peeled off the fatigue test piece, two or three minutes after affixing, and was recovered. Gold was vapor-deposited on the recovered replica film, and the fatigue cracks in the test area were observed with a metallurgical microscope.

30 [0049] The site of a target fatigue crack could thus be observed even though the test piece was not observed directly. In the case of a hydrogen-charged material, a sample 7 mm in diameter and 0.8 mm thick was sliced from the test area immediately after the end of fatigue testing, was placed in a vacuum chamber, and was heated at a constant temperature rise rate. The vacuum chamber internal pressure was 1×10^{-7} to 3×10^{-7} Pa before the sample was heated. The temperature rise rate in the vacuum chamber was 0.33°C/s or 0.5°C/s.

35 [0050] Heating the sample in the vacuum chamber caused hydrogen to desorb from the sample. The amount of desorbed hydrogen was measured using a quadrupole mass analyzer-type thermal desorption analyzer (hereinafter, TDS). The TDS used for measurement was a thermal desorption analyzer (hereafter, TDS) EMD-WA1000S/H by ESCO, Ltd. (location: Musashino, Tokyo, Japan). The precision of the TDS measurement was 0.01 wt ppm.

[Measured properties]

45 [0051] Fig. 5 is a photograph of fatigue cracks that developed from the artificial microhole drilled in hydrogen-uncharged SUS304 after fatigue testing. The photograph shows fatigue cracks spreading from the artificial microhole. These fatigue cracks develop bilaterally from the artificial microhole, and propagate in a roughly symmetrical manner. Figs. 6A and 6B are graphs illustrating the relationship between the number of cycles in the fatigue test and crack length of the fatigue cracks in the fatigue test pieces as a result of fatigue testing. The ordinate axis in the graphs of Figs. 6A and 6B represents crack length.

50 [0052] The abscissa axis in the graphs illustrated in Figs. 6A and 6B represents the number of cycles in the fatigue test. Figs. 6A and 6B correspond to an instance in which there was used the fatigue test piece having a 7 mm-diameter test area illustrated in Fig. 3A. Fig. 6A corresponds to an instance where the material was SUS304. Fig. 6B corresponds to an instance where the material was SUS316L. The graphs illustrated in Figs. 6A and 6B depict measurement results for both hydrogen-charged pieces and hydrogen-uncharged pieces, for each material SUS304 and SUS316L. The cycling frequency was 1 Hz or 1.2 Hz for SUS304, and 1 Hz for SUS316L. The cycling frequency is virtually unaffected by the difference between 1 Hz and 1.2 Hz.

55 [0053] The graph illustrated in Fig. 6A indicates that a fatigue test piece subjected to cathodic hydrogen-charging and having a hydrogen concentration gradient identical to that of Fig. 1 exhibits a faster fatigue crack growth rate than when

not subjected to hydrogen charging, in a test performed in the atmosphere. For example, the number of cycles N until the crack length $2a$ reaches $400\ \mu\text{m}$ is smaller in a material subjected to cathodic hydrogen charging than in an uncharged material. In these cases, the fatigue crack growth rate is approximately twice as fast in the pieces subjected to cathodic hydrogen charging. The results do not depend on the hydrogen charging method, i.e. cathodic hydrogen charging.

5 **[0054]** In SUS304, where the test was carried out by switching to a 0.68 MPa hydrogen gas atmosphere when the crack length $2a$ reached $200\ \mu\text{m}$, the fatigue crack growth rate became faster as compared with that when the test was carried out in the atmosphere, also in the case of a test piece not subjected to hydrogen charging. By contrast, SUS304 having a total hydrogen concentration of 70.4 wt ppm and 89.2 wt ppm, through exposure to hydrogen gas in experimental examples of the present invention, exhibited a markedly slower fatigue crack growth rate as compared with the afore-
10 mentioned hydrogen-uncharged material and cathodically hydrogen-charged material.

[0055] The Vickers hardness of SUS304, in which the total hydrogen concentration had been raised to 89.2 wt ppm, was 192, i.e. 1.09 times the Vickers hardness 176 in the absence of hydrogen charging. The Vickers hardness herein is measured under a test load of 9.8 N, at room temperature, in the atmosphere. In SUS304 having the total hydrogen concentration raised to 70.4 wt ppm through exposure to hydrogen gas, the fatigue crack growth rate exhibits no noticeable
15 difference between a test performed in the atmosphere and a test performed in a 0.68 MPa hydrogen gas. Sufficient enhancing effect on fatigue strength characteristics is thus obtained also when the material is used in a hydrogen environment.

[0056] Fig. 6B illustrates measurement results of SUS316L subjected to a fatigue test in the atmosphere. Fatigue crack growth rate is slower in a case where the total hydrogen concentration of the test piece is 47 wt ppm, as compared
20 with a test piece not charged with hydrogen. The number of cycles N until the crack length $2a$ reaches $400\ \mu\text{m}$ is greater in the case of hydrogen charging to 30 wt ppm or higher, than in the absence of hydrogen charging. The fatigue crack growth rate is about 8 times slower in the case of hydrogen charging to 30 wt ppm or higher.

[0057] Fig. 7A and Fig. 7B are graphs illustrating the relationship between crack length in a fatigue test piece and number of cycles in a fatigue test. The fatigue test piece is a test piece having a 4 mm-diameter test area illustrated in
25 Fig. 3B. Fatigue testing of the fatigue test piece was carried out in the atmosphere. The graph of Fig. 7A illustrates measurement results of a fatigue test of a test piece where the material is SUS304, in a case where the test piece is charged with hydrogen, and a case where not. The cycling frequency in the fatigue test was 0.3 Hz. The graph of Fig. 7B illustrates measurement results of a fatigue test using a test piece where the material is SUS316L, in a case where
30 the test piece is charged with hydrogen, and a case where not.

[0058] The cycling frequency in the fatigue test is 0.3 Hz until the crack length $2a$ reaches about $400\ \mu\text{m}$, and 0.05 Hz thereafter. In the case of Fig. 7A, where the total hydrogen concentration of the fatigue test piece is 23.8 wt ppm and there is no region where the local hydrogen concentration is 30 wt ppm or higher (SUS304), the number of cycles N until the crack length $2a$ reaches $1000\ \mu\text{m}$ is reduced by about 4/5 and the fatigue crack growth rate becomes faster,
35 vis-à-vis a case where no hydrogen charging is carried out (SUS304).

[0059] In the case of a total hydrogen concentration of 98.6 wt ppm of the present invention (SUS304), by contrast, no fatigue cracks derived from the artificial microhole are formed by the stage where the number of cycles at which the crack length $2a$ reaches $1000\ \mu\text{m}$ is $N=11000$ in case of no hydrogen charging. This indicates that development of fatigue cracks is suppressed. In the fatigue test piece (SUS316L) having a total hydrogen concentration of 78.9 wt ppm,
40 as illustrated in Fig. 7B, the number of cycles N until the crack length $2a$ reaches $1000\ \mu\text{m}$ is about 8 times greater than that when no hydrogen charging is carried out (SUS316L). This is indicative of significantly enhanced fatigue crack growth resistance in the fatigue test piece.

[0060] Fig. 8 illustrates the relationship between the test stress amplitude σ and the fatigue life N_f at which the fatigue test piece fractures in the SUS304 material having an artificial microhole. The ordinate axis of the graph represents stress amplitude and the abscissa axis represents fatigue life. In a comparison of fatigue life at a stress amplitude of
45 280 MPa, the test piece containing 89.2 wt ppm of total hydrogen concentration exhibits a fatigue life that is about 8 times longer than that of a test piece not charged with hydrogen. In a fatigue test piece containing 109 wt ppm of total hydrogen concentration, no fatigue cracks develop even at about 27 times the number of cycles of the fatigue life of the fatigue test piece that is not charged with hydrogen.

[0061] The Vickers hardness of the fatigue test piece having a total hydrogen concentration of 109 wt ppm was 193, namely 1.10 times the Vickers hardness 176 of the fatigue test piece not charged with hydrogen. As a characterizing
50 feature of the invention, the austenitic stainless steel of the present invention is charged with hydrogen to 30 wt ppm or more. Occurrence of fatigue cracks in the austenitic stainless steel is dramatically reduced by incorporating 30 wt ppm or more of hydrogen into the austenitic stainless steel. Fatigue crack growth in the austenitic stainless steel can likewise be dramatically slowed down by incorporating 30 wt ppm or more of hydrogen into the austenitic stainless steel.

[0062] It can be easily inferred that fewer fatigue cracks, and/or resistance against fatigue crack growth, should allow
55 prolonging the fatigue life of the austenitic stainless steel, but fatigue crack growth is accelerated a case where the region at which the local hydrogen concentration is 30 wt ppm or higher is located about several tens of μm from the surface and the local hydrogen concentration further inward is less than 30 wt ppm, as in the graph of Fig. 1.

[0063] The number of cycles until the crack length $2a$ reaches $300\ \mu\text{m}$ takes up half the fatigue life, as illustrated in Figs. 6A and 6B. Therefore, fatigue strength characteristics can be effectively enhanced if the local hydrogen concentration is 30 wt ppm or higher in a region at least at a depth of $100\ \mu\text{m}$ or deeper, for a crack length $2a = 300\ \mu\text{m}$. Preferably, the austenitic stainless steel has a local hydrogen concentration of 50 wt ppm or higher.

[0064] An explanation follows next on the alloying components in the austenitic stainless steel of the present invention, on the content of the alloying components, and on a manufacturing method as prescribed by the manufacturing method of the present invention.

Austenitic stainless steel

[0065] Austenitic stainless steel, also called Cr-Ni stainless steel, is obtained through addition of Cr and Ni to Fe. The main components of austenitic stainless steel are Fe, Cr and Ni, with various additives given in Table 2 below.

[0066] Table 2 below shows preferred examples of the austenitic stainless steel of the present invention, but the way in which the present invention is embodied is in no way limited thereto.

Table 2

Component	Composition 1 (weight ratio)	Composition 2 (weight ratio)
C	0.030 or less	0.08 or less
Si	1.00 or less	1.50 or less
Mn	2.00 or less	2.00 or less
Ni	12.00 to 15.00	8.00 to 27.00
Cr	16.00 to 18.00	13.50 to 26.00
Mo	2.00 to 3.00 or less	3.00 or less
Al	-	0.35 or less
N	-	0.50 or less
Ti	-	2.35 or less
V	-	0.50 or less
B	-	0.010 or less
H	0.00007 (0.7 ppm) or less	0.00007 (0.7 ppm) or less
Other	Balance Fe and unavoidable impurities	Balance Fe and unavoidable impurities

Composition of the austenitic stainless steel

[0067] Cr is added to Fe to improve corrosion resistance. Ni is added to Fe, in combination with Cr, to increase corrosion resistance. Ni and Mn are elements for securing non-magnetism after cold rolling. The Ni content must be 10.0wt% or higher to secure non-magnetism after cold rolling. In addition, the content of Ni must be adjusted in accordance with the content of Si and Mn, in such a manner so as to preclude formation of a mechanically-induced martensitic phase of 1vol% or greater. Mn also has the effect of improving the solid solubility of N.

[0068] C is an element used for forming strong austenite. In addition, C is an effective element for enhancing the strength of stainless steel. When an excess of C is added, coarse Cr carbides precipitate during a recrystallization process, and intergranular corrosion resistance and fatigue characteristics are impaired. Si is added for deacidification and strengthening of the solid solution. Adding only a small amount of Si is preferred, since formation of the martensitic phase during cold-working is promoted by the Si content. N brings solution hardening about.

[0069] Mo is added for improving corrosion resistance and has also the effect of bringing about a fine dispersion of carbonitrides in an aging treatment. Ti is an effective element for precipitation hardening, and is added to increase the strength brought about by the aging treatment. B is an effective alloying component for preventing edge cracks in the hot-rolled steel area caused by the difference in deformation resistance between the δ -ferrite phase in the hot working temperature region and in the austenitic phase. Al is an element added for deacidification during steelmaking, and is effective in precipitation hardening, in a manner similar to Ti.

[0070] The present invention can also be embodied by adding elements such as Nb, Cu or the like, as needed, besides

the elements described in Table 2 above. Nb can serve as a substitute for Ti.

Austenitic phase

5 **[0071]** In a preferred austenitic stainless steel, the austenitic phase is essentially 100% of the total volume. Austenitic stainless steel having no martensitic phase is preferred. Instances of abundant martensitic phase with respect to austenitic phase, for instance as in Non-patent document 2, do not fall under the definition of austenitic stainless steel according to the present invention.

10 Other properties

[0072] The average grain size is preferably about 50 μm or less. In modern materials the average grain size is about 50 μm , but a smaller average grain size is preferred.

15 Hydrogenation treatment by heating

[0073] An explanation follows next on a hydrogenation treatment of austenitic stainless steel by heating. Incorporating 30 wt ppm or more of hydrogen into an austenitic stainless steel is effective in enhancing resistance against fatigue crack generation and/or growth. This effect of hydrogen has been found for the first time by the inventors of the present invention. To bring that effect about, 30 wt ppm or more of hydrogen is added into austenitic stainless steel by carrying out a thermal treatment as follows.

20 **[0074]** The austenitic stainless steel is subjected to a thermal treatment at a heating temperature of 80°C or higher to add diffusible hydrogen and non-diffusible hydrogen. The thermal treatment is carried out in a hydrogen environment. Hydrogen environments include, for instance, high-pressure and low-pressure hydrogen gas environments, cathodic hydrogen charging environments, immersion hydrogen charging environments, as well as liquid-phase or gas-phase environments having a high partial pressure of hydrogen. In the thermal treatment, the austenitic stainless steel is kept at the heating temperature for up to 460 hours in the hydrogen environment. The heating temperature is preferably lower than the sensitization temperature, which is the temperature at which chromium (Cr) carbides in the austenitic stainless steel precipitate by heating.

25 **[0075]** In the case of the austenitic stainless steels of Table 1 and Table 2, for instance, the upper limit of the heating temperature is 500°C. Preferably, the thermal treatment is performed at a heating temperature not lower than 200°C in order to add hydrogen effectively into a surface layer over a thickness of 100 μm or greater from the surface. By way of such a thermal treatment, diffusible hydrogen and non-diffusible hydrogen, which cause hydrogen embrittlement in austenitic stainless steel, are added to the austenitic stainless steel in an amount of 30 wt ppm or more. The content of hydrogen (H) in the austenitic stainless steel becomes thus 0.0030 wt% (30 wt ppm) or greater.

30 **[0076]** The amount of hydrogen (H) contained in the austenitic stainless steel after the thermal treatment is preferably 0.0050 wt% (50 wt ppm) or higher. An austenitic stainless steel having excellent fatigue strength characteristics, in which occurrence and/or growth of fatigue cracks are suppressed, can be provided by increasing thus the amount of hydrogen contained in austenitic stainless steel beyond conventional amounts.

35

40 Other experimental examples 1

[0077] Hydrogenation treatment experiments were carried out using test pieces made of SUS316(A), SUS316L(B), SUS310S(A) and SUH660(A). The test pieces were 7 mm-diameter round bars. In the experiments, the test pieces were subjected to a 200-hour thermal treatment at a temperature of 280°C in hydrogen gas at a pressure of 94 MPa. The total hydrogen concentration and the Vickers hardness of the test pieces after the thermal treatment were measured. For TDS measurement, the test pieces were sliced into discs having a diameter of 7 mm and a thickness of 0.8 mm.

45 **[0078]** The TDS used for measurement was a thermal desorption analyzer EMD-WA1000S/H by ESCO, Ltd. (location: Musashino, Tokyo, Japan). The measurement results are given in Table 3. The hydrogen concentration in the test pieces not subjected to the hydrogenation treatment ranged from 1.5 to 3.4 wt ppm. The hydrogen concentration in the test pieces subjected to the thermal treatment in the hydrogen gas environment ranged from 69.9 to 129.1 wt ppm. The change in Vickers hardness from before the hydrogenation treatment to Vickers hardness after the hydrogenation treatment ranged from 1.08-fold to 1.11-fold.

50

55

Table 3

Hydrogenation treatment conditions	Hydrogen concentration (weight ppm)/Vickers hardness				Remarks
	SUS316(A)	SUS316(B)	SUS310S(A)	SUH660(A)	
94 MPa hydrogen gas, heating temperature 280°C, held for 200 hours	95.7/175	87.7/157	129.1/146	69.9/-	Example of the present invention
102 MPa hydrogen gas, heating temperature 120°C, held for 120 hours	79.4/-	73.6/-	-/-	-/-	Example of the present invention
Hydrogen-uncharged material	3.4/161	1.5/145	2.8/132	1.2/-	Comparative example

Other experimental examples 2

[0079] Hydrogenation treatment experiments were carried out using test pieces made of SUS316(A) and SUS316L (B). The fatigue test pieces were discs having a diameter of 7 mm and a thickness of 0.2 mm. In the experiments, the test pieces were subjected to a 120-hour thermal treatment at a temperature of 120°C in hydrogen gas at a pressure of 102 MPa. The total hydrogen concentration of the fatigue test piece of SUS316(A) before the hydrogen charging treatment was 3.4 wt ppm. The total hydrogen concentration of the fatigue test piece after the hydrogen charging treatment was 79.4 wt ppm. The total hydrogen concentration of the fatigue test piece of SUS316L(B) before the hydrogen charging treatment was 1.5 wt ppm.

[0080] The total hydrogen concentration of the fatigue test piece after the hydrogen charging treatment was 73.6 wt ppm. Fig. 11 illustrates the relationship between hydrogen concentration in the entire fatigue test piece and Vickers hardness ratio. The Vickers hardness ratio denotes herein the ratio of Vickers hardness of austenitic stainless steel subjected to the hydrogen charging treatment of the present invention with respect to 1, which is the Vickers hardness of austenitic stainless steel containing only unavoidable hydrogen taken up during a conventional manufacturing process. As Table 1 shows, austenitic stainless steels obtained by conventional manufacturing methods comprise ordinarily 1 to 5 wt ppm of hydrogen.

[0081] The concentration of hydrogen in stainless steel can be thus brought to 30 wt ppm or higher by subjecting the stainless steel to a thermal treatment in the above-described hydrogen environments. The hydrogen environment of the present invention is not limited to a high-pressure hydrogen gas environment. The hydrogen charging treatment may also be performed in an environment suitable for hydrogen charging achieved by controlling the environment at which manufacturing processes, for instance a solution thermal treatment, are carried out. The saturation concentration of hydrogen in a metallic material such as stainless steel is determined experimentally and/or theoretically on the basis of, for instance, the metal material, the hydrogen charging treatment method, as well as the temperature, pressure and so forth during the hydrogen charging treatment. For instance, the hydrogen saturation concentration of SUS316 and SUS316L is about 100 ppm in a hydrogen charging treatment in an environment at 100 MPa and 280°C. Similarly, the hydrogen saturation concentration of SUS310S is about 120 ppm in a hydrogen charging treatment in an environment at 280°C. Therefore, charging at or beyond the saturation concentration of hydrogen is technically meaningless, and hence the hydrogen charging treatment of the present invention refers to charging up to the hydrogen saturation concentration.

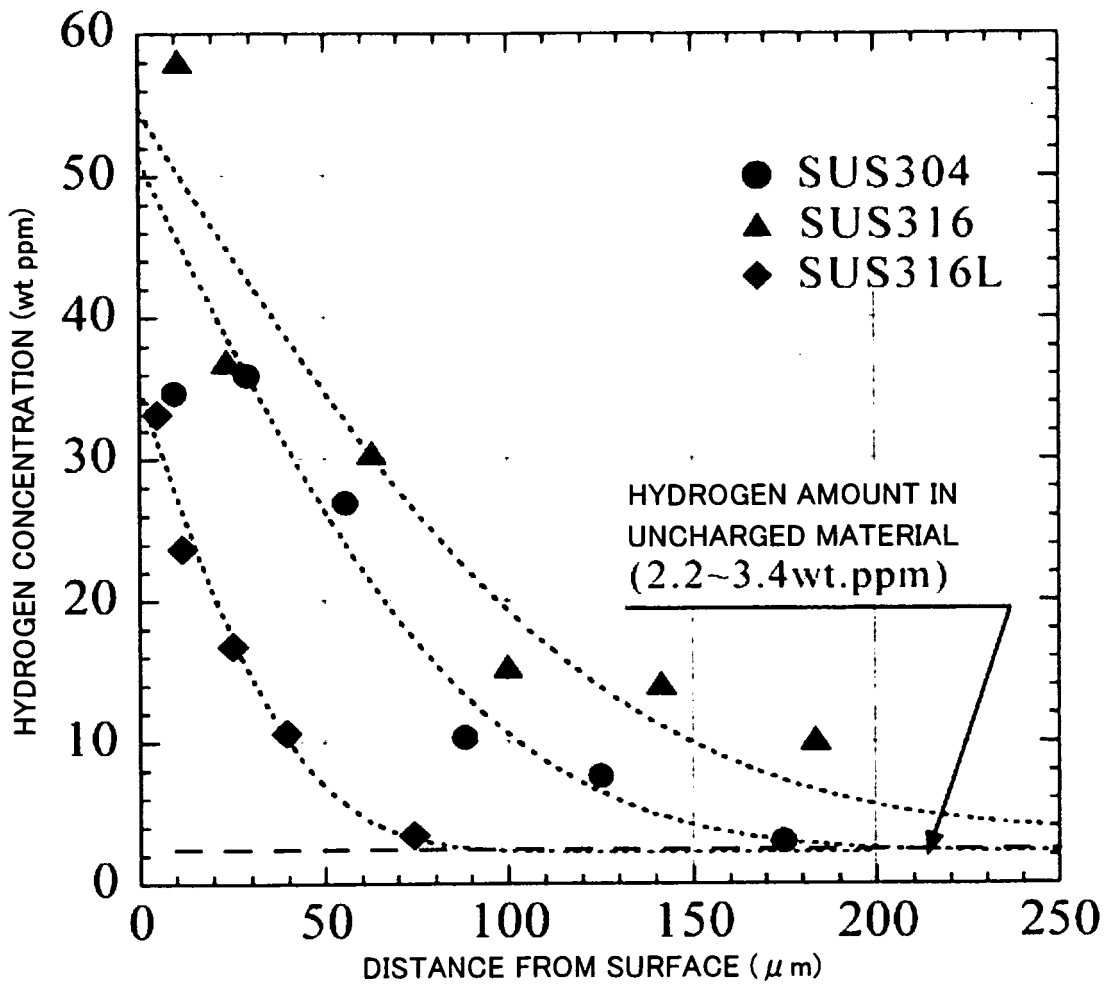
INDUSTRIAL APPLICABILITY

[0082] The present invention is good for use in corrosion resistance and in fields that employ high-pressure hydrogen. In particular, the present invention may be appropriate for use in members that may undergo hydrogen embrittlement and/or delayed fracture due to hydrogen intrusion, for instance metal gaskets, various types of valves used in automobiles, springs, piping, flexible hoses, couplings, pressure gauges, diaphragms, bellows, pressure containers, bolts, steel belts, cutting blades, fuel cells, as well as materials for valves, springs and the like ancillary to fuel cell systems.

Claims

1. An austenitic stainless steel having an austenitic phase the crystalline structure of which is a face-centered cubic lattice structure,
5 wherein the austenitic stainless steel undergoes a manufacturing process such that a region in which a concentration of hydrogen (H) comprising diffusible hydrogen and non-diffusible hydrogen contained in the austenitic stainless steel is locally 0.0030 wt% (30 wt ppm) or higher has a thickness of 100 μm or more from the surface of the austenitic stainless steel into the austenitic stainless steel, and wherein occurrence of fatigue cracks in the austenitic stainless steel is delayed, and/or growth of the fatigue cracks is slowed down.
10
2. The austenitic stainless steel according to claim 1, wherein the concentration of the hydrogen (H) in the entirety of the austenitic stainless steel has a value of 0.0030 wt% (30 wt ppm) or higher.
3. The austenitic stainless steel according to claim 1, wherein the concentration of the hydrogen (H) is 0.0050 wt%
15 (50 wt ppm) or higher.
4. The austenitic stainless steel according to claim 2, wherein the concentration of the hydrogen (H) in the entirety of the austenitic stainless steel has a value of 0.0050 wt% (50 wt ppm) or higher.
- 20 5. The austenitic stainless steel according to any one of claims 1 to 4, wherein the Vickers hardness (HV) of the austenitic stainless steel is 1.05 or higher, 1 being the Vickers hardness (HV) of an austenitic stainless steel in which the concentration of the hydrogen (H) in the entirety of the austenitic stainless steel is 0.0005 wt% (5 wt ppm) or less.
- 25 6. The austenitic stainless steel according to any one of claims 1 to 5, wherein the hydrogen is stored in the austenitic stainless steel by subjecting the austenitic stainless steel to a thermal treatment at a heating temperature of 80°C or higher in a hydrogen environment.
- 30 7. The austenitic stainless steel according to claim 6, wherein the heating temperature ranges from 200°C to 500°C.
8. An austenitic stainless steel hydrogenation method of adding hydrogen to an austenitic stainless steel, in order to increase the concentration of hydrogen in an austenitic stainless steel having an austenitic phase the crystalline structure of which is a face-centered cubic lattice structure, the method comprising the step of:
35 heating the austenitic stainless steel at a heating temperature of 80°C or higher in a hydrogen environment, to cause thereby a region in which a local concentration of the hydrogen contained in the austenitic stainless steel is 0.0030 wt% (30 wt ppm) or higher to be formed to a thickness of 100 μm or more from the surface of the austenitic stainless steel into the austenitic stainless steel.
- 40 9. The austenitic stainless steel hydrogenation method according to claim 8, wherein the hydrogen is stored in the austenitic stainless steel by keeping the austenitic stainless steel for up to 460 hours at a temperature ranging from 200°C to 500°C, being a temperature lower than a sensitization temperature at which chromium (Cr) carbides in the austenitic stainless steel precipitate by heating.
- 45 10. The austenitic stainless steel hydrogenation method according to claim 8 or 9, wherein an overall concentration of the hydrogen (H) contained in the austenitic stainless steel is 0.0030 wt% (30 wt ppm) or higher.
- 50 11. The austenitic stainless steel hydrogenation method according to claim 8 or 9, wherein the local concentration of the hydrogen (H) contained in the austenitic stainless steel is 0.0050 wt% (50 wt ppm) or higher.
- 55 12. The austenitic stainless steel hydrogenation method according to claim 10, wherein the overall concentration of the hydrogen (H) contained in the austenitic stainless steel is 0.0050 wt% (50 wt ppm) or higher.

Fig.1



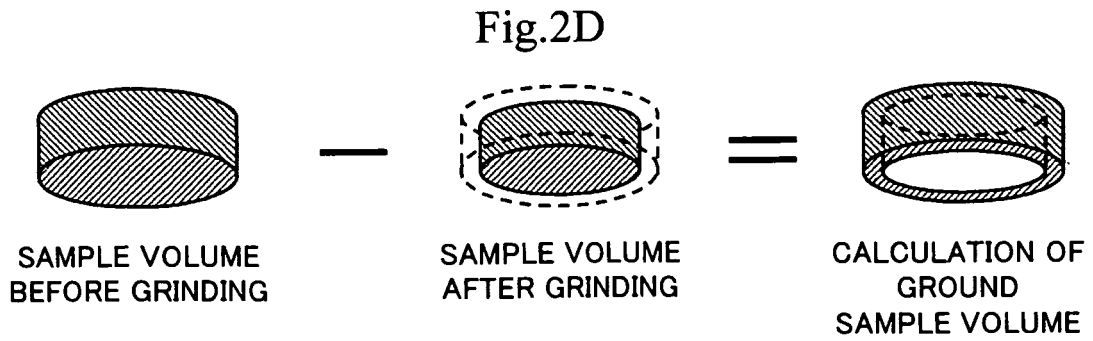
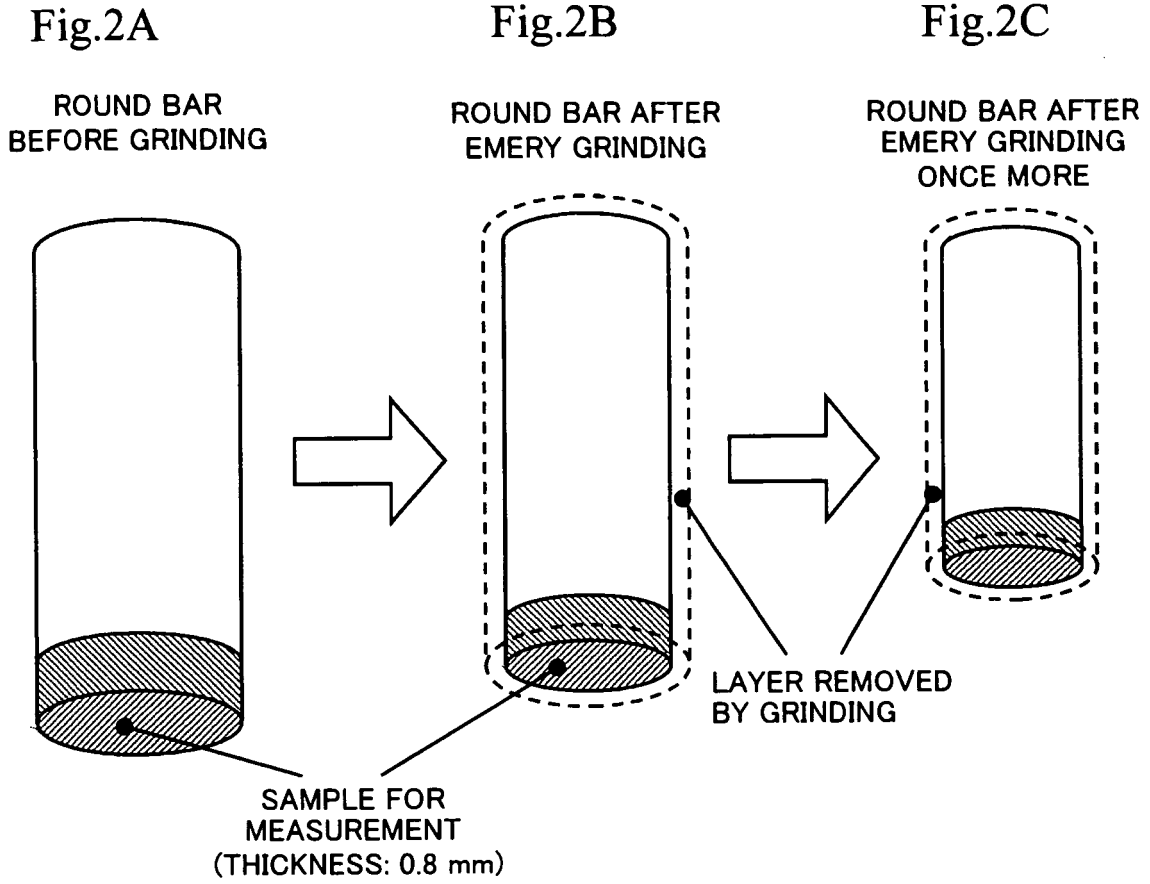


Fig.3A

Fatigue test piece. Example 1

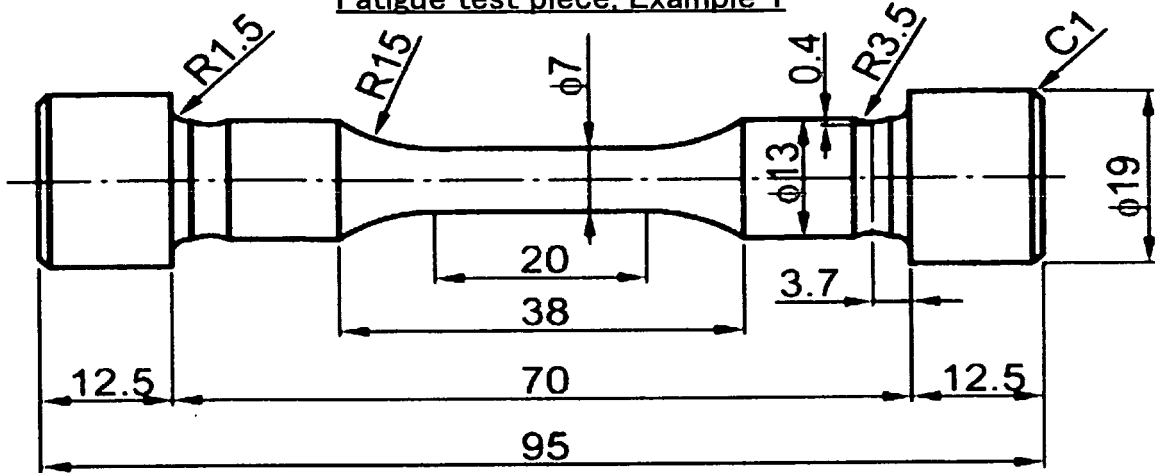


Fig.3B

Fatigue test piece. Example 2

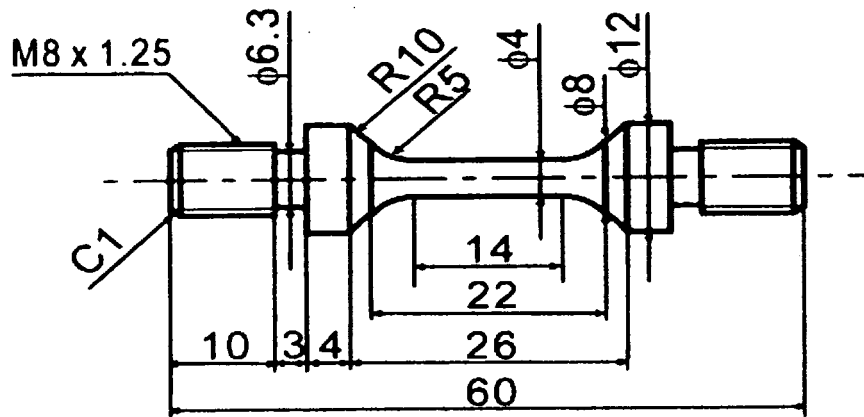


Fig.3C

Artificial microhole

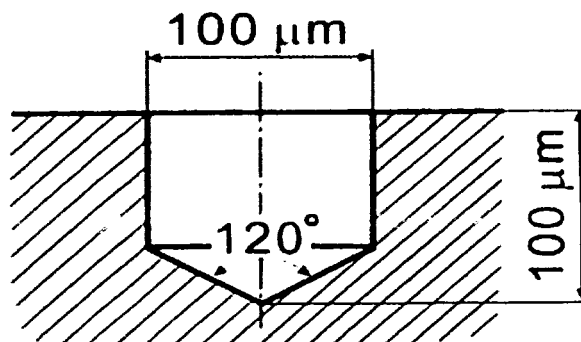


Fig.4

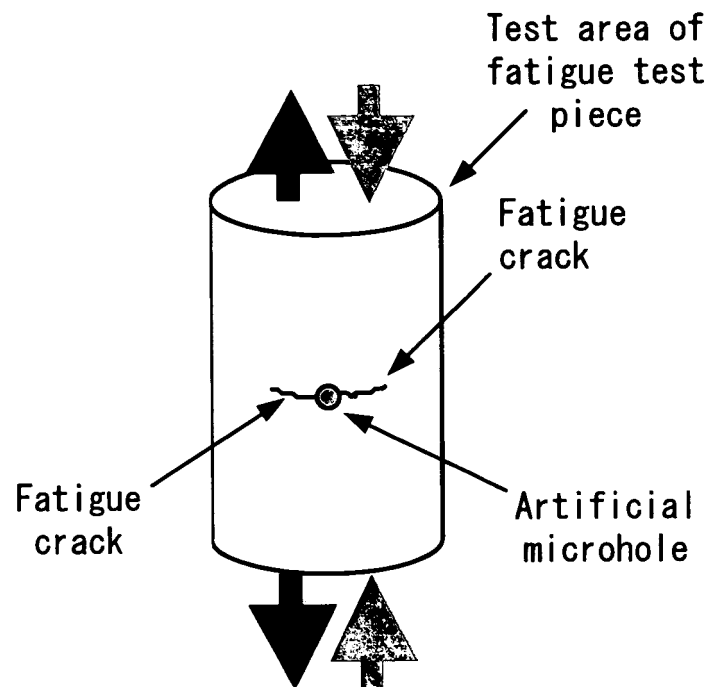


Fig.5



Fig.6A

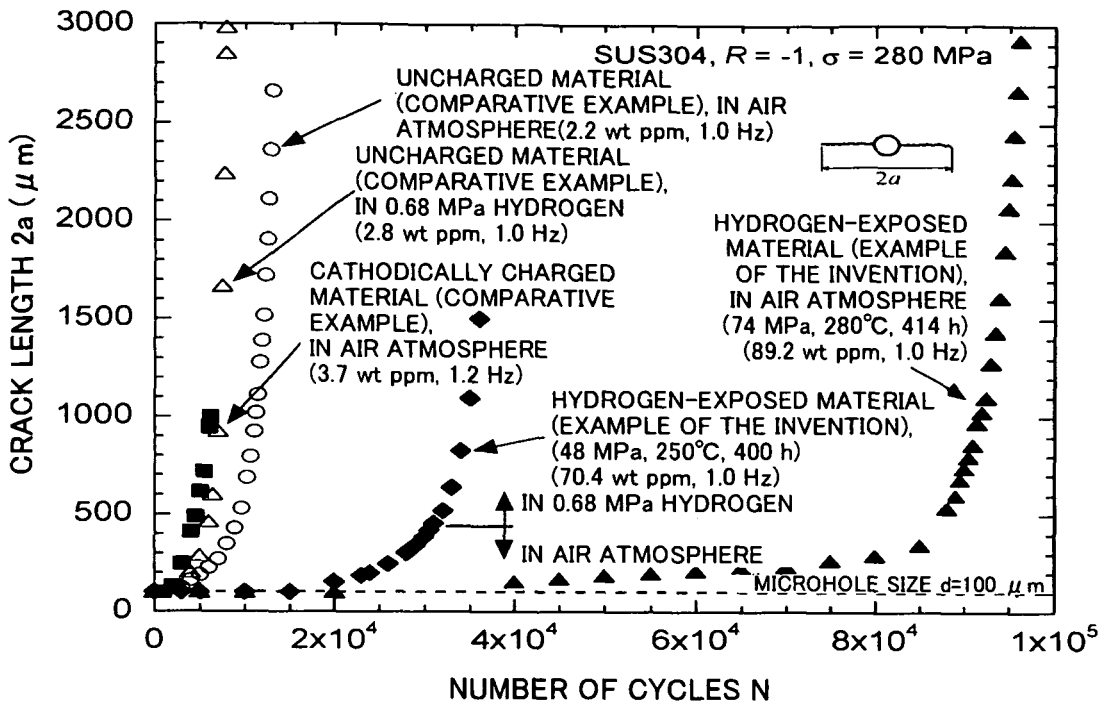


Fig.6B

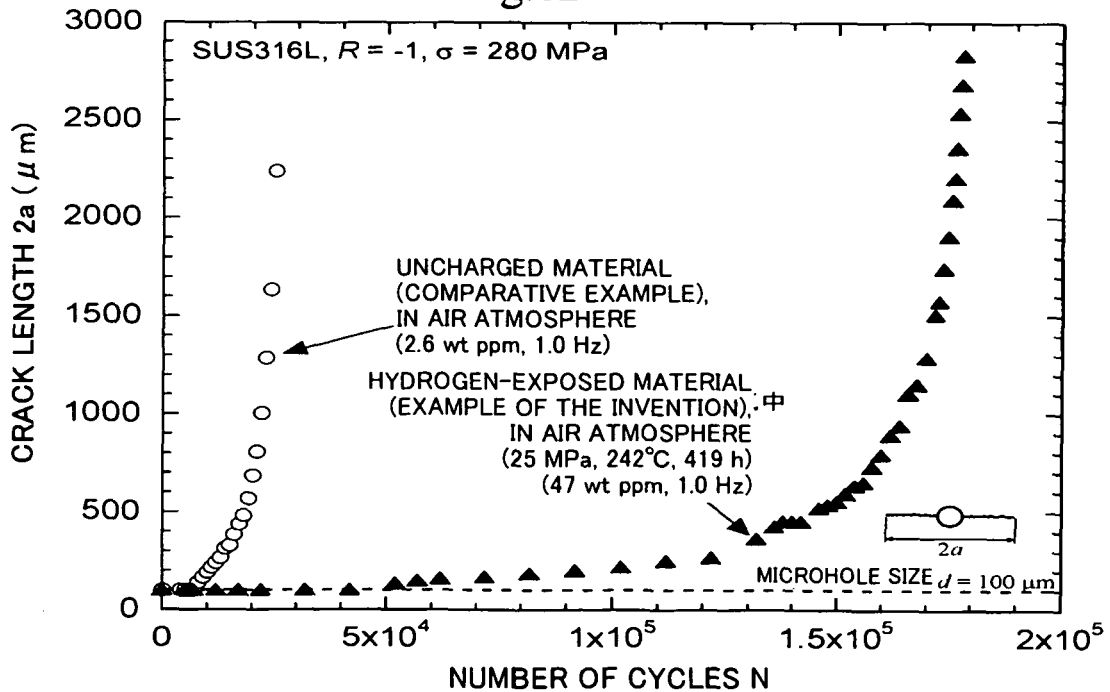


Fig.7A

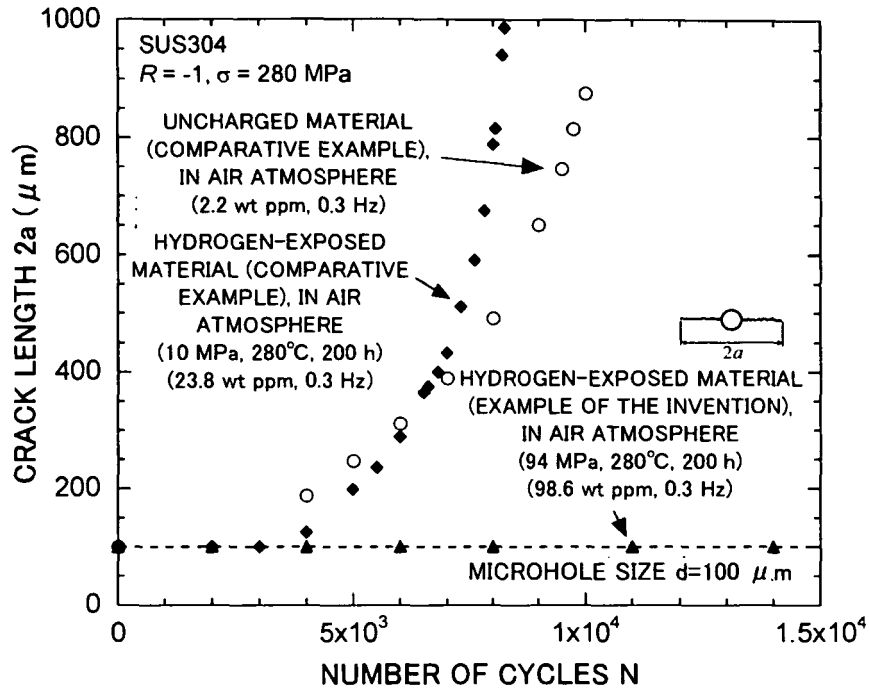


Fig.7B

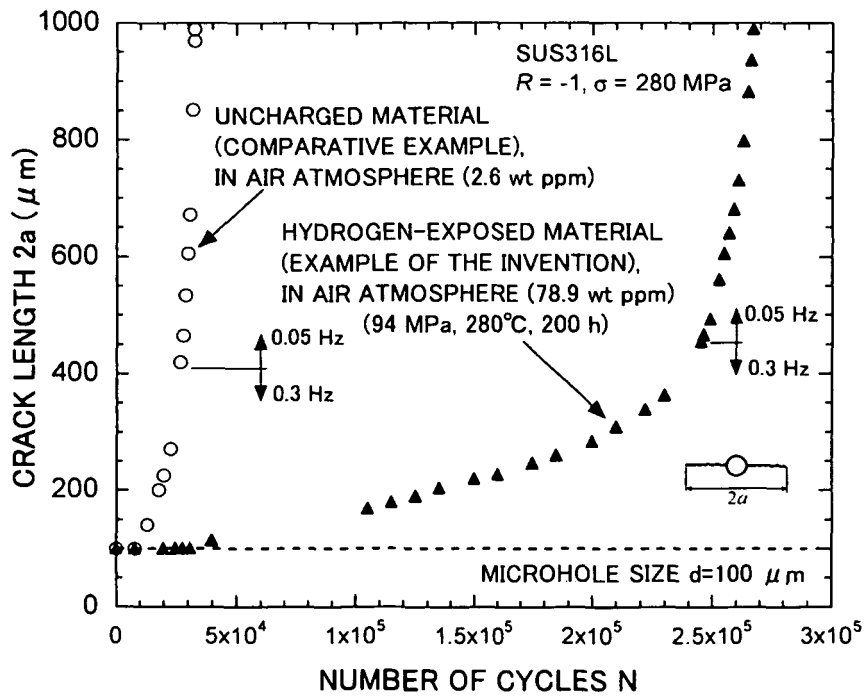


Fig.8

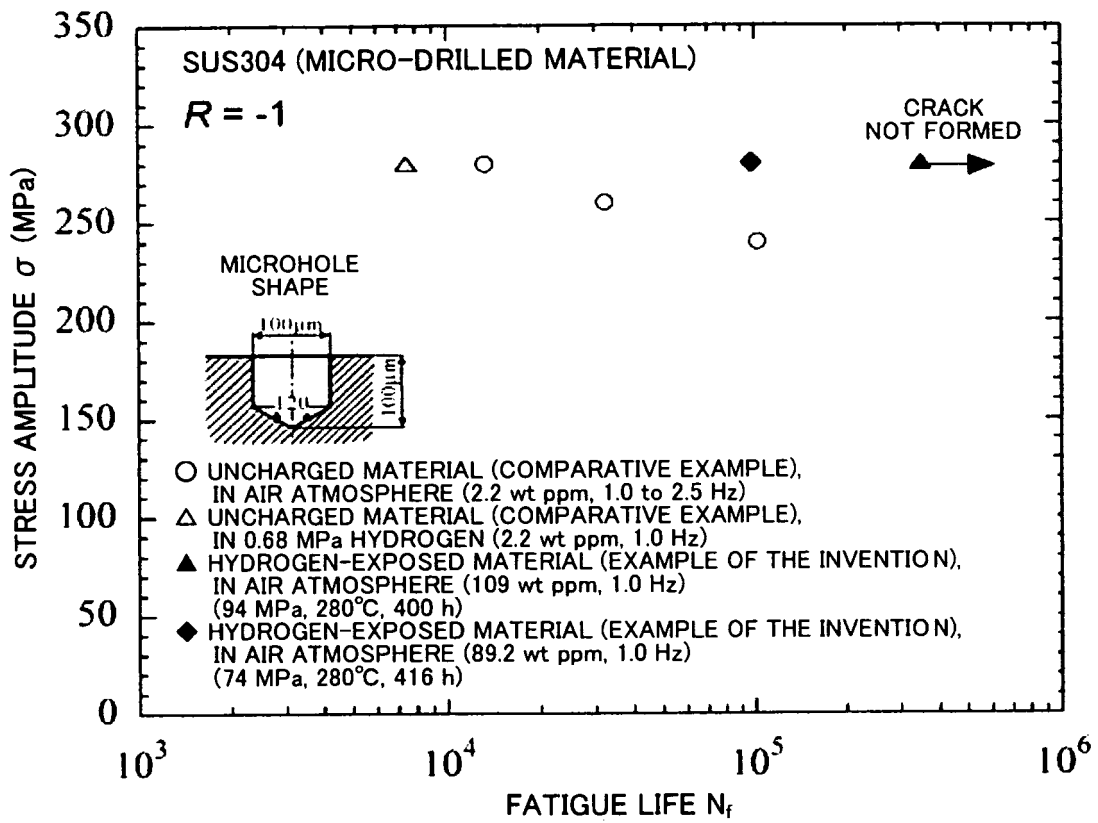


Fig.9A

Face centered cubic lattice
(FCC)

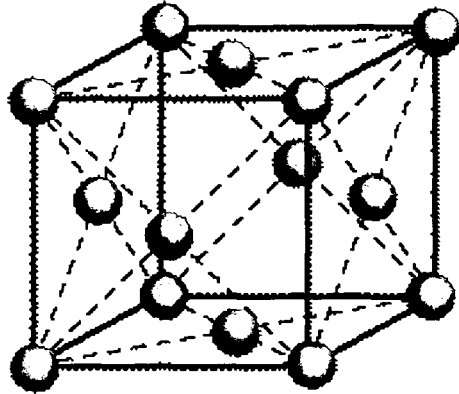


Fig.9B

Body centered cubic lattice
(BCC)

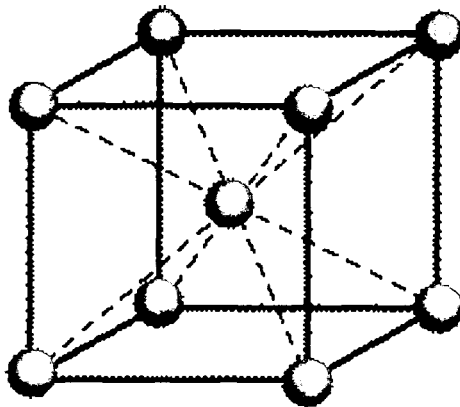


Fig.10

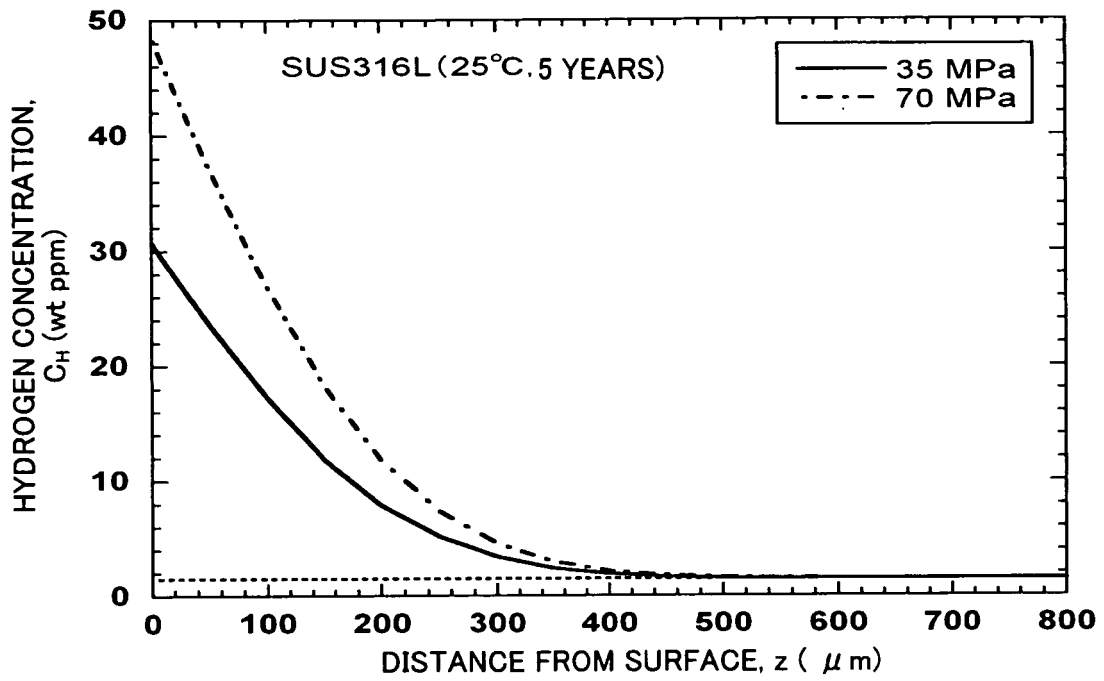
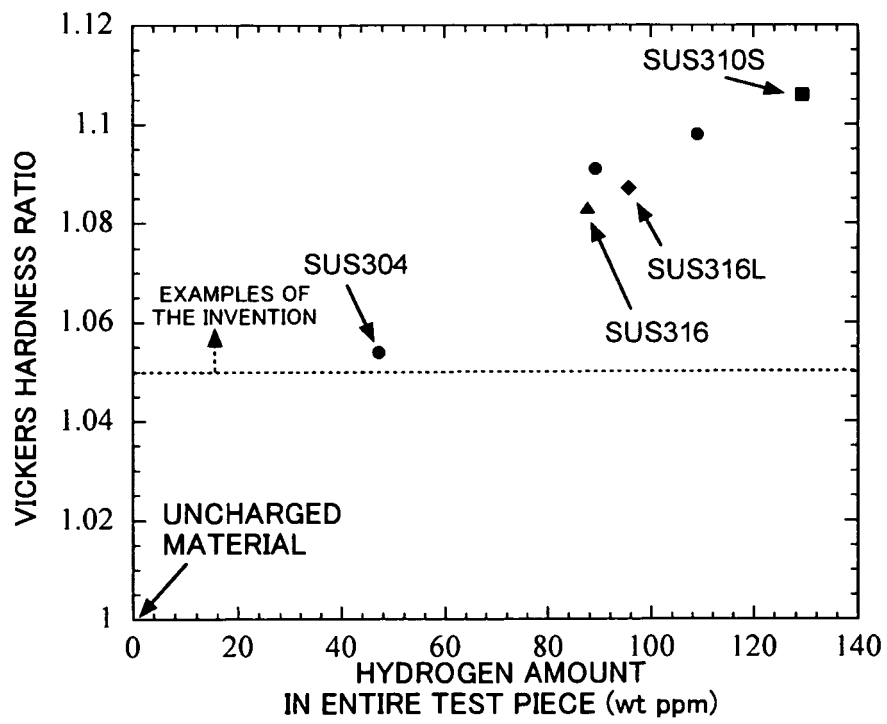


Fig.11



INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2009/062970

<p>A. CLASSIFICATION OF SUBJECT MATTER C22C38/00(2006.01)i, C22C38/58(2006.01)i, C21D6/00(2006.01)i</p> <p>According to International Patent Classification (IPC) or to both national classification and IPC</p>																													
<p>B. FIELDS SEARCHED</p> <p>Minimum documentation searched (classification system followed by classification symbols) C22C38/00, C21D6/00, C22C38/58</p> <p>Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Jitsuyo Shinan Koho 1922-1996 Jitsuyo Shinan Toroku Koho 1996-2009 Kokai Jitsuyo Shinan Koho 1971-2009 Toroku Jitsuyo Shinan Koho 1994-2009</p> <p>Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)</p>																													
<p>C. DOCUMENTS CONSIDERED TO BE RELEVANT</p> <table border="1"> <thead> <tr> <th>Category*</th> <th>Citation of document, with indication, where appropriate, of the relevant passages</th> <th>Relevant to claim No.</th> </tr> </thead> <tbody> <tr> <td>A</td> <td>JP 2007-126688 A (Nippon Steel & Sumikin Stainless Steel Corp.), 24 May 2007 (24.05.2007), paragraphs [0002] to [0008] & US 2009/0159602 A1 & EP 1944385 A1 & WO 2007/052773 A1</td> <td>1-12</td> </tr> <tr> <td>A</td> <td>JP 06-049538 A (Nippon Nuclear Fuel Development Co., Ltd.), 22 February 1994 (22.02.1994), paragraphs [0002] to [0005] (Family: none)</td> <td>1-12</td> </tr> </tbody> </table> <p><input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.</p> <table border="0"> <tr> <td>* Special categories of cited documents:</td> <td>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</td> </tr> <tr> <td>"A" document defining the general state of the art which is not considered to be of particular relevance</td> <td>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</td> </tr> <tr> <td>"E" earlier application or patent but published on or after the international filing date</td> <td>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</td> </tr> <tr> <td>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</td> <td>"&" document member of the same patent family</td> </tr> <tr> <td>"O" document referring to an oral disclosure, use, exhibition or other means</td> <td></td> </tr> <tr> <td>"P" document published prior to the international filing date but later than the priority date claimed</td> <td></td> </tr> </table> <table border="1"> <tr> <td>Date of the actual completion of the international search 08 October, 2009 (08.10.09)</td> <td>Date of mailing of the international search report 20 October, 2009 (20.10.09)</td> </tr> <tr> <td>Name and mailing address of the ISA/ Japanese Patent Office</td> <td>Authorized officer</td> </tr> <tr> <td>Facsimile No.</td> <td>Telephone No.</td> </tr> </table>			Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.	A	JP 2007-126688 A (Nippon Steel & Sumikin Stainless Steel Corp.), 24 May 2007 (24.05.2007), paragraphs [0002] to [0008] & US 2009/0159602 A1 & EP 1944385 A1 & WO 2007/052773 A1	1-12	A	JP 06-049538 A (Nippon Nuclear Fuel Development Co., Ltd.), 22 February 1994 (22.02.1994), paragraphs [0002] to [0005] (Family: none)	1-12	* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention	"A" document defining the general state of the art which is not considered to be of particular relevance	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone	"E" earlier application or patent but published on or after the international filing date	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art	"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&" document member of the same patent family	"O" document referring to an oral disclosure, use, exhibition or other means		"P" document published prior to the international filing date but later than the priority date claimed		Date of the actual completion of the international search 08 October, 2009 (08.10.09)	Date of mailing of the international search report 20 October, 2009 (20.10.09)	Name and mailing address of the ISA/ Japanese Patent Office	Authorized officer	Facsimile No.	Telephone No.
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.																											
A	JP 2007-126688 A (Nippon Steel & Sumikin Stainless Steel Corp.), 24 May 2007 (24.05.2007), paragraphs [0002] to [0008] & US 2009/0159602 A1 & EP 1944385 A1 & WO 2007/052773 A1	1-12																											
A	JP 06-049538 A (Nippon Nuclear Fuel Development Co., Ltd.), 22 February 1994 (22.02.1994), paragraphs [0002] to [0005] (Family: none)	1-12																											
* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention																												
"A" document defining the general state of the art which is not considered to be of particular relevance	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone																												
"E" earlier application or patent but published on or after the international filing date	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art																												
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&" document member of the same patent family																												
"O" document referring to an oral disclosure, use, exhibition or other means																													
"P" document published prior to the international filing date but later than the priority date claimed																													
Date of the actual completion of the international search 08 October, 2009 (08.10.09)	Date of mailing of the international search report 20 October, 2009 (20.10.09)																												
Name and mailing address of the ISA/ Japanese Patent Office	Authorized officer																												
Facsimile No.	Telephone No.																												

INTERNATIONAL SEARCH REPORT

International application No. PCT/JP2009/062970
--

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, A	JP 2008-208451 A (National Institute of Advanced Industrial Science and Technology), 11 September 2008 (11.09.2008), claims; paragraphs [0001] to [0017] & CA 2649355 A1 & WO 2008/093453 A1	1-12

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- JP 2004339569 A [0009]
- JP H10199380 B [0009]
- JP 2005009955 A [0009]

Non-patent literature cited in the description

- **Toshihiko KANEZAKI ; Chihiro NARAZAKI ; Yoji MINE ; Saburo MATSUOKA ; Yukitaka MURAKAMI.** The effect of hydrogen on fatigue crack growth of prestrained austenitic stainless steel. *The Japan Society of Mechanical Engineers [No. 05-9] Proceedings of the 2005 Annual Meeting of JSME/MMD, M&M*, 04 November 2005, vol. P86, 595-596 [0009]
- **Toshihiko KANEZAKI ; Chihiro NARAZAKI ; Yoji MINE ; Saburo MATSUOKA ; Yukitaka MURAKAMI.** Martensitic transformation and effect of hydrogen on fatigue crack growth in stainless steels. *Transactions of the Japan Society of Mechanical Engineers A*, 01 May 2006, vol. 72 (723), 123-130 [0009]
- **Yukitaka MURAKAMI ; Toshihiko KANEZAKI ; Yoji MINE ; Saburo MATSUOKA.** Hydrogen Embrittlement Mechanism in Fatigue of Austenitic Stainless Steels. *Metallurgical and Materials Transactions A*, 25 November 2007, vol. 39A, 1327-1339 [0009]