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(54) **AUSTENITIC STAINLESS STEEL AND PROCESS FOR HYDROGEN REMOVAL THEREOF**

(57) The present invention focuses on diffusible hydrogen and non-diffusible hydrogen that cause hydrogen embrittlement in an austenitic stainless steel, and provides the austenitic stainless steel having diffusible hydrogen and non-diffusible hydrogen removed therefrom, and a method for removing hydrogen therefrom. In order

to remove diffusible hydrogen and non-diffusible hydrogen, which cause hydrogen embrittlement in the austenitic stainless steel, an aging treatment is performed to the austenitic stainless steel at a temperature ranging from 200 to 1100°C while being kept in an air atmosphere. As a result, the hydrogen (H) content in the austenitic steel is removed to 0.001 wt% (1 wt ppm) or less.

Fig. 14A

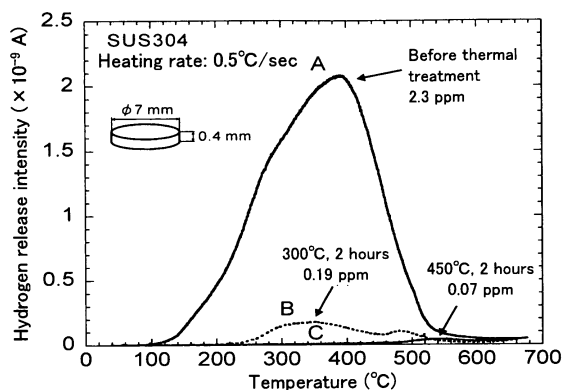
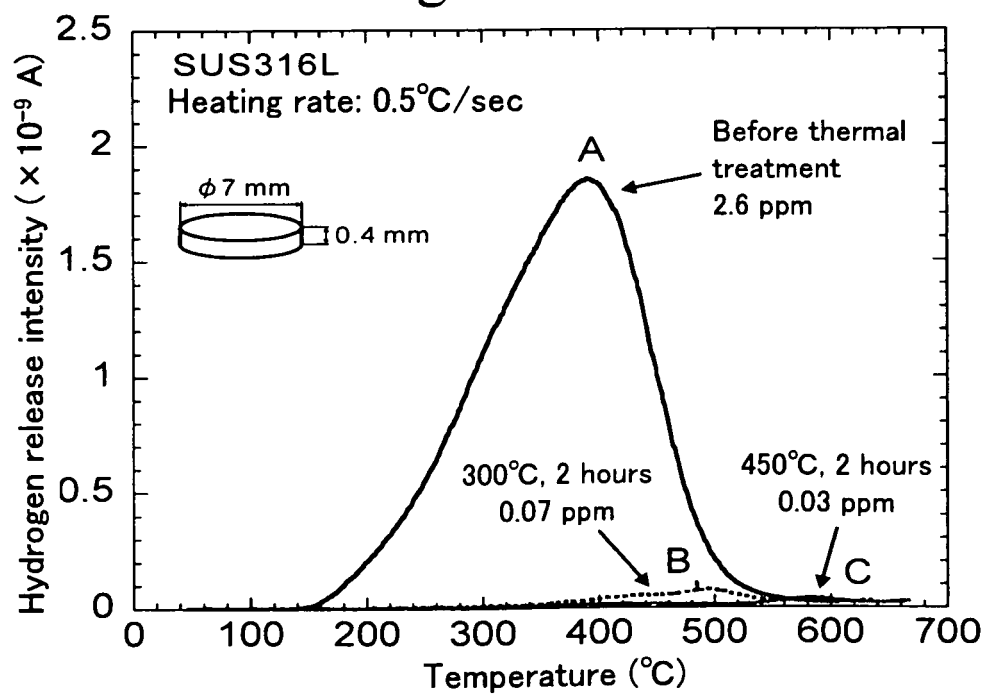


Fig. 14B



DescriptionTECHNICAL FIELD

5 **[0001]** The present invention relates to an austenitic stainless steel having reduced hydrogen embrittlement and to a method for removing hydrogen therefrom. More specifically, the present invention relates to an austenitic stainless steel wherein there is a reduced influence of hydrogen present therein on the growth of fatigue cracks that occur in the austenitic stainless steel, and to a method for removing hydrogen therefrom.

10 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. An important subject that has become the target of attention, in particular, is the development and practical application of stationary fuel cells, fuel cell-powered vehicles and the like that utilize hydrogen as fuel. 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 already 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 amounts of the components expressed in wt %. The content of hydrogen (H) is expressed as wt ppm (parts per million by weight).

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Table 1

(Component units: wt %, *wt ppm)												
	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] It is known that hydrogen penetrates into metallic materials and decreases the static strength and fatigue strength thereof (Non-patent Documents 1 and 2). Various methods for removing such hydrogen, and methods for predicting the effect of hydrogen, have been proposed. In Patent Document 2, for example, an 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 more, to remove the hydrogen and prevent hydrogen embrittlement. Patent document 3 discloses a method wherein the extent of hydrogen embrittlement of an austenitic stainless steel is predicted and judged based on the chemical composition thereof.

[0005] Patent Documents 4 and 5 disclose austenitic stainless steel wires that are subjected to a dehydrogenation treatment. Patent Document 4 (Table 2 and paragraphs [0015] to [0016]) discloses a high-strength austenitic stainless steel wire having 1.5 ppm or less of hydrogen, as a result of a dehydrogenation treatment (300°C for 24 hours). The stainless steel wire does not exhibit drawing longitudinal cracking in a tensile test, at tensile strengths from 1900 N/mm² to about 2200 N/mm². The wire has a content of mechanically-induced martensite of 30 to 75% after drawing.

[0006] Patent Document 5 (Table 2, paragraph [0042]) discloses a high-strength austenitic stainless steel wire in which the hydrogen content is reduced to 1.5 ppm through a dehydrogenation treatment (low-temperature aging at 400°C for 30 minutes). The stainless steel wire does not break in a tensile test, at tensile strengths from 2000 N/mm² to 2800 N/mm². The wire has a content of mechanically-induced martensite of 25 to 75% after drawing. The inventions disclosed in Patent Documents 4 and 5, however, are inventions of austenitic stainless steel wire, and disclose nothing as regards fatigue testing under slow cycling frequency.

[0007] 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 with their hydrogen-charged counterparts. 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 with SUS316L.

[0008] 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 the uncharged counterpart. The fatigue crack growth rate is accelerated two-fold in SUS316L.

[0009] However, even a semi-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 overturn this common belief. This finding is the more significant in that the results were obtained by applying cyclic loading at a low frequency of 5 Hz or less.

[0010] Specifically, it has been shown that the growth rate of fatigue cracks is accelerated by low-frequency cyclic loading in an austenitic stainless steel such as SUS316L. Meanwhile, Non-patent Document 2 points out the following: "(3) The martensitic phase resulting from transformation in the austenitic stainless steel becomes a pathway for hydrogen diffusion throughout the material, and the diffusion coefficient of hydrogen is increased thereby" (see page 130).

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

Patent Document 4: Japanese Patent Application Laid-open No. H10-121208

Patent Document 5: Japanese Patent Application Laid-open No. 2005-298932

Non-patent Document 1: Toshihiko KANEZAKI, Chihiro NARAZAKI, Yoji MINE, Saburo MATSUOKA, and Yukitaka MURAKAMI: The effect of hydrogen on fatigue crack growth of pre-strained austenitic stainless steel. The Japan Society of Mechanical Engineers [No. 05-9] Proceedings of the 2005 Annual Meeting of JSME/MMD, Vol. 2005 (Nov. 4 to 6, 2005, Fukuoka city) P. 86, p. 595 to 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), p. 123 to 130 (manuscript received: May 1, 2006)

[0011] At present, however, sufficient analysis is still lacking on how non-diffusible hydrogen, which is present in crystals, 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.

[0012] 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, loading and release are repeated

in a relatively slow cycle that involves, for instance, the filling of the high-pressure hydrogen container with hydrogen gas and the subsequent consumption thereof. In the past, however, fatigue tests have not taken this slow cycle into account. Specifically, it was thought that fatigue testing under quick cycling frequencies could stand for fatigue tests under long-cycle loads.

[0013] Low-frequency cyclic loading occurs also due to, for instance, temperature variations in the outside air temperature. A conceivable example of cyclic loading due to variations in the outside air temperature is, for instance, thermal stress resulting from compression and expansion of the stainless steel itself, and of the parts connected to stainless steel components, as a result of temperature differences between day and night. As for the frequency of the cycle, the temperature difference between day and night can range from only a few degrees to ten degrees centigrade or more, and one cycle is 24 hours long. This means that high pressure hydrogen tanks in fuel cell vehicle-related facilities, high-pressure hydrogen tanks, facilities for supplying fuel for fuel cells, and the like have a cycle measured in single day units as noted above, and the hydrogen fill time is 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

[0014] The present invention is based on the above technical background, and attains the following objects.

An object of the present invention is to provide an austenitic stainless steel for reducing the influence of hydrogen on the growth rate of fatigue cracks that occur in the austenitic stainless steel, and to provide a method for removing the hydrogen therefrom.

A further object of the present invention is to provide an austenitic stainless steel in which diffusible hydrogen and non-diffusible hydrogen are removed therefrom, and to provide a method for removing the hydrogen therefrom, by focusing on diffusible hydrogen and non-diffusible hydrogen that cause hydrogen embrittlement in the austenitic stainless steel.

[0015] A further object of the present invention is to provide an austenitic stainless steel in which diffusible hydrogen and non-diffusible hydrogen are removed therefrom, and to provide a method for removing the hydrogen therefrom, by focusing on diffusible hydrogen and non-diffusible hydrogen that become problematic under cyclic loading with a long cycle time.

A further object of the present invention is to provide an austenitic stainless steel wherein diffusible hydrogen and non-diffusible hydrogen that are present in the austenitic stainless steel are removed therefrom during a manufacturing step of the austenitic stainless steel, and to provide a method for removing the hydrogen therefrom.

[0016] A further object of the present invention is to provide an austenitic stainless steel wherein diffusible hydrogen and non-diffusible hydrogen that are present in the austenitic stainless steel are removed therefrom during a manufacturing step of the austenitic stainless steel, in particular during a thermal treatment in an air atmosphere, and to provide a method for removing the hydrogen from the austenitic stainless steel.

A further object of the present invention is to provide an austenitic stainless steel that allows slowing down the growth rate of fatigue cracks during repeated low-frequency loading, and to provide a method for removing the hydrogen from the austenitic stainless steel.

Definition of terms

[0017] The present invention uses the following technical terms in the meanings defined below. "Hydrogen charging" means 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 and the like. "Fatigue crack growth" refers to the enlargement of defects and cracks that occur in a material, as a result of cyclic loading, during the manufacturing process, or cracks from bores, holes and the like that are artificially opened into the material.

[0018] Fatigue crack growth rate denotes the rate at which a fatigue crack progresses. An 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 and exhibiting increased corrosion resistance in corrosive environments and the like. Table 1 gives a list of such stainless steels. An austenitic phase denotes 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 lattice structure).

[0019] Fig. 11A 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 lattice structure). Fig. 11B 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 temperatures.

[0020] This transformation from an austenitic phase with an FCC structure to a martensitic phase with a BCC structure by cold working is called 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. Diffusible hydrogen causes hydrogen embrittlement in the material. Hydrogen that cannot escape from the material over time even at temperatures from room temperature to about 200°C, is called non-diffusible hydrogen.

[0021] The present invention achieves the above objects on the basis of the following means.

The inventors of the present invention found that non-diffusible hydrogen in an austenitic stainless steel is related to fatigue crack growth, and on the basis of this finding, the inventors invented an austenitic stainless steel and a method for removing hydrogen therefrom. The present invention relates to an austenitic stainless steel having an austenitic phase whose crystalline structure is a face-centered cubic lattice structure, and to a method for removing hydrogen from the austenitic stainless steel.

[0022] The austenitic stainless steel of the present invention has an austenitic phase where a crystalline structure is a face-centered cubic lattice structure, and the austenitic stainless steel is subjected to a thermal treatment in an air atmosphere, at a heating temperature ranging from 200°C to 1100°C, to remove thereby diffusible hydrogen and non-diffusible hydrogen that cause hydrogen embrittlement in the austenitic stainless steel, and remove a content of hydrogen (H) in the austenitic stainless steel to 0.0001 wt% (1.0 wt ppm) or less.

[0023] A method for removing hydrogen from an austenitic stainless steel of the present invention comprises a step of heating the austenitic stainless steel, having an austenitic phase where a crystalline structure is a face-centered cubic lattice structure, in an air atmosphere, at a heating temperature ranging from 200°C to 1100°C, to remove thereby diffusible hydrogen and non-diffusible hydrogen in the austenitic stainless steel, to a content of 0.0001 wt% (1.0 wt ppm) or less.

[0024] The diffusible hydrogen and the non-diffusible hydrogen that are removed in accordance with the method for removing hydrogen from an austenitic stainless steel of the present invention diffuse via a mechanically-induced martensitic phase, brought about by cyclic loading at low-frequency, accumulate in cracks that are under stress concentration, increase thereby the growth rate of fatigue cracks, and cause hydrogen embrittlement in the austenitic stainless steel.

[0025] The explanation below applies to the austenitic stainless steel and the method for removing hydrogen therefrom of the present invention. In the austenitic stainless steel of the present invention, preferably, the diffusible hydrogen and the non-diffusible hydrogen in the austenitic stainless steel are removed so that the hydrogen (H) in the austenitic stainless steel is 0.00007 wt% (0.7 wt ppm) or less. In the austenitic stainless steel of the present invention, more preferably, the diffusible hydrogen and the non-diffusible hydrogen in the austenitic stainless steel are removed so that the hydrogen (H) in the austenitic stainless steel is 0.00002 wt% (0.2 wt ppm) or less.

[0026] To remove the diffusible hydrogen and the non-diffusible hydrogen, the austenitic stainless steel is subjected to a thermal treatment at a heating temperature of 200°C or higher in an air atmosphere. Preferably, the upper limit of the heating temperature is 1100°C, and in particular, the temperature of the thermal treatment is lower than the sensitization temperature, which is the temperature at which carbides of chromium (Cr) in the austenitic stainless steel precipitate due to heating. The duration of the thermal treatment ranges from 2 hours to 500 hours.

[0027] The diffusible hydrogen and the non-diffusible hydrogen diffuse via a mechanically-induced martensitic phase brought about by cyclic loading at low-frequency, accumulate in cracks that are under stress concentration, increase thereby the growth rate of fatigue cracks, and cause hydrogen embrittlement in the austenitic stainless steel.

[0028] Removal of diffusible hydrogen and non-diffusible hydrogen from the austenitic stainless steel of the present invention may be carried out in a dedicated step for removal. Preferably, however, removal is performed not in a separate step but in the manufacturing process of the austenitic stainless steel, in the form of a thermal treatment for a predetermined duration to remove hydrogen to a hydrogen (H) content of 0.00007 wt% (0.7 wt ppm) or less. The manufacturing process of the austenitic stainless steel can be streamlined as a result, since there is included no special process for removing diffusible hydrogen and non-diffusible hydrogen. Preferably, the temperature in the thermal treatment is 200°C or higher but lower than the melting point temperature of the stainless steel.

[0029] The duration of heating in the manufacturing process varies depending on the volume of the material, but ranges in practice from 2 hours to several tens of hours. The manufacturing process takes place preferably in an inert gas flow atmosphere. Conceptually, the manufacturing process of an austenitic stainless steel includes herein a solution thermal treatment and an aging treatment that are used in the manufacture of stainless steel.

[0030] In the case of a solution thermal treatment, the temperature in the thermal treatment is most preferably of 920°C or higher. In the case of an aging treatment, the temperature in the thermal treatment is most preferably 700°C or higher. Although not limited to the stainless steels given in Table 1, the stainless steel of the present invention is preferably an austenitic stainless steel or a heat-resistant austenitic steel.

[0031] If the austenitic stainless steel of the present invention is subjected to an aging treatment in the atmosphere, an appropriate heating temperature range is found to be 200 to 1100°C. The rationale for this range is as follows. As shown in Fig. 14A and Fig. 14B in the below-described Additional experimental example 3, hydrogen is released at a temperature of 200°C or higher. This indicates that the stainless steel must be heated at a temperature equal to or higher

than a lowest temperature of 200°C, i.e. indicates that there is a lower limit to the heating temperature. The upper limit of the heating temperature is a temperature below the melting point of the stainless steel.

[0032] Austenitic stainless steels contain ordinarily more hydrogen than 1 ppm in conventional steelmaking methods. The amount of hydrogen depends on the size of the material upon shipping. Fig. 15 is a graph illustrating the relationship between material size and the amount of hydrogen in the material of Table 1. The graph plots the results of measurements performed by the inventors of the present invention on various materials purchased from material manufacturers. The horizontal axis in the graph represents the size of the material. The size denotes herein the smallest value of the material dimensions upon shipping.

[0033] For instance, in a round bar having a diameter of 20 mm $\times$ length 1 m, the size corresponds to the diameter of 20 mm, while in a plate having a width of 200 mm $\times$ plate thickness of 10 mm $\times$ length 1 m, the size corresponds to the plate thickness of 10 mm. In a round bar having a diameter of 20 mm $\times$ length 10 mm, the size corresponds to the length of 10 mm. The above heating times denote the time required for hydrogen to diffuse out of a sample. This time depends on the size of the material. The heating time can be estimated through calculations based on the diffusion coefficient of hydrogen in the material at the heating temperature. Samples of a smaller size can be thermally treated in a shorter time, of several hours.

[0034] Samples of a larger size, by contrast, need a fairly prolonged treatment period, of 2 weeks or more. A heating time longer than the time required for hydrogen to diffuse out of the sample results arguably in no change in the amount of hydrogen, no matter how long the heating time. Therefore, although the effective range of aging treatment time depends on the heating temperature and sample size, it is found that 500 hours or less is a practical range. The aging treatment time, however, is not limited thereto. As Fig. 15 shows, a greater amount of hydrogen is present in a case where there is used a large material, for instance structural materials for power plants and the like, owing to the large material size.

[0035] Such materials are thermally treated with removal of hydrogen in mind, since hydrogen is a cause of embrittlement as ascertained by the inventors of the present invention. Crack growth characteristics are effectively improved by reducing the hydrogen content in the large-size material to 1 ppm or less, through heating. This should translate into more improved stability of building structures, machinery, plants and equipment in which such materials are used. Needless to say, the same effect is elicited in stainless steel of small and very small sizes.

[0036] The present invention affords the following effect. In the present invention, an austenitic stainless steel is thermally treated at a temperature of 200°C or higher, in an air atmosphere, to remove non-diffusible hydrogen and diffusible hydrogen that are present in the austenitic stainless steel, thereby making it possible to provide an austenitic stainless steel that is highly resistant to fatigue crack growth.

BRIEF DESCRIPTION OF THE DRAWINGS

[0037]

Figs. 1A and 1B are diagrams illustrating a fatigue test piece, wherein Fig. 1A is a diagram illustrating the shape of the fatigue test piece, and Fig. 1B is a diagram illustrating the shape of an artificial microhole formed in the fatigue test piece;

Fig. 2 shows a diagram of 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 growing therefrom;

Fig. 3 is a schematic diagram of the procedure for applying prestrain to a fatigue test piece;

Fig. 4 is a photograph of fatigue cracks arising from the artificial microhole after fatigue testing;

Figs. 5A-5C are sets of graphs illustrating results of X-ray examination of the austenitic phase and martensitic phase in the test area surface, before fatigue testing, and the fatigue-cracked surface after fatigue testing, wherein Fig. 5A shows the measurement results for SUS304, Fig. 5B shows the measurement results for SUS316, and Fig. 5C shows the measurement results for SUS316L;

Figs. 6A-6C are sets of graphs illustrating the relationship between the length of the cracks caused by fatigue testing and number of cycles, wherein Fig. 6A shows the results for SUS304, Fig. 6B for SUS316, and Fig. 6C for SUS316L;

Fig. 7 is a set of photographs of fatigue cracks in SUS304, SUS316, and SUS316L observed by the replica method;

Fig. 8 is a graph showing the results of fatigue testing of SUS316L;

Fig. 9 is a graph showing the results of fatigue testing of SUS316L;

Fig. 10 is a conceptual diagram illustrating the factors whereby diffusible hydrogen and non-diffusible hydrogen migrate on account of martensitic transformation;

Figs. 11A and 11B are sets of conceptual diagrams illustrating the lattices of the crystalline structures of the austenitic phase and martensitic phase, wherein Fig. 11A shows a face-centered cubic lattice structure (FCC) of the austenitic phase, and Fig. 11B shows a body-centered cubic lattice structure (BCC) of the martensitic phase;

Fig. 12 is a graph showing the results of Additional experimental example 1;

Fig. 13 is a graph showing the results of Additional experimental example 2;

Figs. 14A and 14B are sets of graphs showing the results of Additional experimental example 3, wherein Fig. 14A corresponds to SUS304 and Fig. 14B corresponds to SUS316L; and

Fig. 15 is a graph illustrating the relationship between hydrogen amount and material size.

BEST MODE FOR CARRYING OUT THE INVENTION

[0038] 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 an 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. In the past, practitioners believed that this non-diffusible hydrogen had no effect on hydrogen embrittlement.

[0039] However, the fatigue tests set out below have shown that non-diffusible hydrogen affects hydrogen embrittlement. Hydrogen embrittlement arising from non-diffusible hydrogen has been verified in particular at a low-frequency fatigue testing rate of about 0.0015 Hz (approximately 11 minutes as the repetition time of one cycle). The inventors of the present invention performed the following tests and observed the way in which non-diffusible hydrogen affected the growth rate of fatigue cracks. One example of such experiments is shown herein.

Test piece

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

[0041] As shown in Fig. 1B, an artificial microhole 100 μm in diameter and 100 μm deep was opened in the center of the fatigue test piece in the lengthwise direction with a drill having a radial tip angle of 120°, to facilitate observation of fatigue crack growth. The artificial microhole was drilled in the center of the test area of the test piece. The test area was a cylindrical portion, approximately 20 mm long, at the center of the test piece. The top and bottom faces of the cylinder were parallel to each other and lay perpendicular to the lengthwise axis of the test piece. Fig. 2 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 immediately after hydrogen charging was over, and the artificial microhole was drilled.

X-ray diffraction

[0042] The amount of martensite in the test area of the fatigue test piece of an austenitic stainless steel was measured by X-ray diffraction. X-ray diffraction was performed using a miniature X-ray stress measurement apparatus PSPC-RSF/KM manufactured by Rigaku Corporation (Akishima city, Tokyo, Japan). Quantitative analysis was determined from the integrated intensity ratio of the diffraction peaks of the austenitic phase {220} plane and the martensitic phase {211} plane, using $\text{CrK}\alpha$ rays. In SUS304, SUS316, and SUS316L the content of martensite in the test area before fatigue testing was about 3%.

[0043] The content of martensite in the hydrogen-charged test areas was also 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 defined by rotating the lengthwise axis of the test piece 180° 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 cylinder from the first measurement region.

Hydrogen charging method

[0044] Hydrogen charging was performed using a cathodic charging method. The hydrogen charging conditions included an aqueous sulfuric acid solution at pH = 3.5, a platinum anode, and a current density of $i = 27 \text{ A/m}^2$. Hydrogen charging was performed for 672 hours (4 weeks) at a solution temperature of 50°C (323 K), and 336 hours (2 weeks) at a solution temperature of 80°C (353 K). The sulfuric acid solution was replaced once a week to minimize changes in the sulfuric acid concentration resulting from evaporation.

Prestrained material

[0045] Prestraining was performed on SUS304 and SUS316L, and martensite-transformed test pieces therefrom were

used to investigate the relationship between the acceleration in fatigue crack growth rate, resulting from hydrogen, and the extent of martensitic transformation. Fig. 3 shows a schematic diagram illustrating the prestraining procedure. Since prestraining promotes martensitic transformation, prestraining was performed in -70°C ethanol. After prestraining, the test piece was worked into a shape such as the one shown in Fig. 1A. Prestraining was applied at a plastic strain (true strain) of $\epsilon_p = 0.28$, for SUS304, and at a plastic strain of $\epsilon_p = 0.35$, for SUS316L.

[0046] The Vickers hardness was measured after prestraining (measurement load of 9.8 N). The measurement yielded HV = 426 (10-point average) for SUS304, and HV = 351 (10-point average) for SUS316L. The variation was within ± 4 . The test piece was polished, and then the amount of martensite in the test area after prestraining was measured by X-ray diffraction. The martensite content was 65 to 69% by specific volume in SUS304, and 26 to 28% by specific volume in SUS316L. The amount of martensite was measured at two places before the artificial microhole was drilled. The measurement regions were 1 mm in diameter centered on the spot where the artificial microhole was to be drilled, and a spot defined by rotating the lengthwise axis of the test piece 180° from the spot where the artificial microhole was to be drilled.

15 Fatigue test method

[0047] The fatigue test used a hydraulic servo-controlled tension and compression fatigue testing machine "Servopulser EHF-ED30KN" manufactured by Shimadzu Corporation (Chukyo-ku, Kyoto), with an cycling frequency of 0.0015 to 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 using the replica method. The length of the fatigue cracks was measured.

[0048] Observation of the fatigue cracks by the replica method revealed the following. An about 0.034 mm-thick acetyl cellulose film (hereinafter, called the replica film) was immersed in methyl acetate liquid for a short time, and was then affixed to the observation site. The replica film was peel off once it had dried, 2 or 3 minutes after affixing. Gold was vapor-deposited on the recovered replica film, and the fatigue cracks in the test area were observed with a metallurgical microscope.

[0049] The location of a target fatigue crack could be observed even if 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 cut out from the test area immediately after the end of fatigue testing, was placed in a vacuum chamber, and was heated at a constant heating rate. The vacuum chamber internal pressure was 1×10^{-7} to 3×10^{-7} Pa before the sample was heated. The temperature was raised up to 800°C at a heating rate of $0.5^{\circ}\text{C}/\text{sec}$.

[0050] Heating the sample in the vacuum chamber caused hydrogen to escape therefrom. The amount of escaped hydrogen was measured with a quadrupole mass analyzer-type thermal desorption spectrometer (hereinafter, TDS). The TDS used for measurement was a thermal desorption spectrometer (EMD-WA1000S/H) manufactured by ESCO, Ltd. (Musashino city, Tokyo, Japan). The precision of the TDS measurement was 0.01 wt ppm.

Measured properties

[0051] Fig. 4 is a photograph of fatigue cracks that developed from the artificial microhole drilled in hydrogen-uncharged SUS304 after fatigue testing. The photograph shows that fatigue cracks spread from the artificial microhole. These fatigue cracks develop bilaterally from the artificial microhole, and grow in a roughly symmetrical manner.

[0052] Figs. 5A-5C show results of X-ray examination of the austenitic phase and martensitic phase in the test area surface before fatigue testing and the fatigue-cracked surface after fatigue testing. The dotted lines in Figs. 5A-5C denote results upon measuring of the surface of the test area before fatigue testing. The solid line denotes results upon measuring fatigue-cracked surface after fatigue testing. Fig. 5A shows the measurement results for SUS304. The measurement indicates that, after fatigue testing, the austenitic phase has decreased and the martensitic phase has increased, as compared with before fatigue testing.

[0053] Fig. 5B shows the measurement results for SUS316. The measurement indicates that, after fatigue testing, the austenitic phase has decreased a little and the martensitic phase has increased, as compared with before fatigue testing. Fig. 5C shows the measurement results for SUS316L. The measurement indicates that, after fatigue testing, the martensitic phase has increased, as compared with before fatigue testing, although virtually no change in the austenitic phase is seen for SUS316L.

[0054] Figs. 6A-6C are graphs showing the relationship between the length of the cracks caused by fatigue testing and number of cycles. Fig. 6A shows the results for SUS304, Fig. 6B for SUS316, and Fig. 6C for SUS316L. The measurement results are shown for hydrogen-charged pieces and uncharged pieces for each material (SUS304, SUS316, and SUS316L). The cycling frequency is 1.2 Hz for SUS304 and SUS316, and 5 Hz for SUS316L.

[0055] The graph indicates that the crack growth rate is accelerated in hydrogen-charged SUS304 and SUS316, as compared with the uncharged material. For example, the number of cycles N until crack length $2a$ reaches $400 \mu\text{m}$ is

lower in a hydrogen-charged material than in the uncharged material. In these cases, the fatigue crack growth rate is approximately twice as fast in the hydrogen-charged pieces. The fatigue crack growth rate for SUS316L is slightly higher in the hydrogen-charged material than in the uncharged material, but no significant difference is appreciated.

[0056] Fig. 7 shows photographs of fatigue cracks in SUS304, SUS316, and SUS316L observed by the replica method. As the photograph in Fig. 4 shows, the fatigue cracks grow essentially symmetrically, and therefore the photographs in Fig. 7 depict only one half of the photograph. The photographs reveal that the fatigue cracks in hydrogen-charged material tend to grow more linearly than in uncharged material. The hydrogen-charged material the slip bands occur over a broad region, whereas in the uncharged material the slip bands are localized near the fatigue cracks.

[0057] Fig. 8 is a graph showing the results of fatigue testing of SUS316L. Fig. 8 shows the fatigue test results of two materials with a hydrogen content of 0.4 wt ppm and 2.6 wt ppm when uncharged, and results after the material with a hydrogen content of 2.6 wt ppm was charged with hydrogen to raise the content thereof to 3.9 wt ppm. The cycling frequency until the fatigue cracks reached a length of 200 μm was 1.5 Hz. Once the length of the fatigue cracks reached 200 μm , the cycling frequency was changed from 1.5 Hz to 0.0015 Hz. The fatigue cracks grew in a material with a hydrogen content of 2.6 wt ppm and 3.9 wt ppm.

[0058] However, fatigue cracks grew only slightly in the material with a hydrogen content of 0.4 wt ppm. Fig. 9 is a graph showing the results of fatigue testing of SUS316L. This figure shows the fatigue test results of two materials with a hydrogen content of 0.4 wt ppm and 2.6 wt ppm when uncharged, and results after the material with a hydrogen content of 2.6 wt ppm was charged with hydrogen to raise the content thereof to 3.9 wt ppm and 5.1 wt ppm. Two cycling frequencies were used, namely 1.5 Hz and 0.0015 Hz.

[0059] The graph indicates that fatigue cracks grow in the material having a hydrogen content of 2.6 wt ppm and in the same material charged with hydrogen to a content of 3.9 wt ppm and 5.1 wt ppm. When the cycling frequency is a low 0.0015 Hz, the fatigue crack growth rate is faster than at a cycling frequency of 1.5 Hz. However, the graph shows that in the material with a hydrogen content of 0.4 wt ppm the fatigue crack growth rate is slower at both cycling frequencies of 0.0015 Hz and 1.5 Hz. This indicates that fatigue cracks do not grow much when the hydrogen content in the material is 0.4 wt ppm or less.

[0060] Fig. 10 is a conceptual diagram illustrating a situation wherein diffusible hydrogen and non-diffusible hydrogen diffuse through a transformed martensitic phase. The tip of the fatigue crack in the figure undergoes martensitic transformation, and the diffusible hydrogen and the non-diffusible hydrogen diffuse via the martensitic phase. That is, hydrogen migrates through a route made up of the martensitic phase, which has a high hydrogen diffusion rate, and accumulates at the tip of the fatigue crack. This phenomenon relates to hydrogen diffusion and migration time. The rate of diffusion of the hydrogen in the austenitic phase (FCC) is four orders of magnitude slower than the rate of diffusion in the martensitic phase (BCC). The fatigue crack periphery undergoes martensitic transformation, and the surrounding hydrogen diffuses through this martensitic phase and gathers at the tip of the fatigue crack.

Involvement of Non-Diffusible Hydrogen

[0061] The above test showed thus that not only diffusible hydrogen, but also non-diffusible hydrogen, which has been disregarded in prior art, is involved in fatigue crack growth. This is a novel finding concerning hydrogen embrittlement. Specifically, martensitic transformation at the fatigue crack tip (transformation from FCC to BCC) affects hydrogen embrittlement.

Relationship between fatigue test rate and fatigue crack growth rate

[0062] As illustrated in Fig. 9 relating to the above experiments, it is found that fatigue crack growth rate accelerates in austenitic stainless steels such as SUS316L when the fatigue test rate is slow. Likewise, as shown in Figs. 6A-6C, the fatigue crack growth rate is faster in a hydrogen-charged material, such as the test pieces charged with diffusible hydrogen, than in an uncharged material. As shown in Figs. 8 and 9, fatigue cracks hardly grow in a material with a hydrogen content of 0.4 wt ppm or less. Thus, the slowing effect on the fatigue test rate is a phenomenon related to hydrogen diffusion and migration time (the diffusion rate is four orders of magnitude slower in FCC than in BCC).

[0063] An explanation follows next on the alloying components in the austenitic stainless steel of the present invention, on the content thereof, and on a manufacturing method as prescribed by the manufacturing method of the present invention.

Austenitic stainless steel

[0064] The austenitic stainless steel is also called Cr-Ni stainless steel, and is obtained through the addition of Cr and Ni to Fe. The principal components of the austenitic stainless steel are Fe (iron), Cr (chromium), and Ni (nickel), with various additives given in Table 2 below.

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[0065] 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 by no means 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 (0.7ppm) or less
Other	Balance Fe and unavoidable impurities	Balance Fe and unavoidable impurities

Austenitic stainless steel

[0066] 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 (manganese) are elements for securing nonmagnetic properties after cold rolling. The Ni content must be 10.0 wt% or more to secure nonmagnetic properties after cold rolling. In addition, the content of Ni must be adjusted in accordance with the content of Si (silicon) and Mn in such a manner so as to preclude generation of a mechanically-induced martensitic phase of 1 vol% or greater. Mn also has the effect of improving the solid solubility of N (nitrogen).

[0067] C (carbon) 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 the recrystallization process, and intergranular corrosion resistance and fatigue properties are impaired. Si is added for deacidification and strengthening of the solid solution. Adding only a small amount thereof is preferred since generation of the martensitic phase during cold-working is promoted by the Si content. Nitrogen brings about solution hardening.

[0068] Mo (molybdenum) is added for improving corrosion resistance. Mo has also the effect of bringing about a fine dispersion of carbonitrides in the aging treatment. Ti (titanium) is an effective element for precipitation hardening, and is added to increase the strength brought about by the aging treatment. B (boron) is an effective alloying component for the prevention of 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 the austenitic phase. Al (aluminum) is an element added for deacidification during steelmaking and is effective in precipitation hardening, in a similar manner to Ti.

[0069] The present invention can also be embodied by adding elements such as Nb, Cu or the like, as needed, in addition to the elements described in Table 2 above. Nb can serve as a substitute for titanium.

Austenitic phase

[0070] The austenitic stainless steel wherein the austenitic phase is essentially 100% of the total volume is preferred. The austenitic stainless steel having no martensitic phase is preferred.

Other properties

[0071] 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 the average grain size is preferred.

Hydrogen removal treatment by heating

[0072] An explanation follows next on a hydrogen removal treatment involving the heating of the austenitic stainless steel. The inventors of the present invention found that non-diffusible hydrogen is involved in fatigue crack growth. On the basis of this finding, the thermal treatment described below is performed to remove non-diffusible hydrogen and diffusible hydrogen that are present in the austenitic stainless steel.

[0073] Removal of the diffusible hydrogen and the non-diffusible hydrogen involves performing a thermal treatment on the austenitic stainless steel at a heating temperature of 200°C or higher. The thermal treatment is performed in a vacuum environment. The vacuum environment is 0.2 Pa or less. In the thermal treatment, the austenitic stainless steel is kept under vacuum at the heating temperature for 460 hours or less. The temperature of the thermal treatment is lower than the sensitization temperature, which is the temperature at which carbides of chromium (Cr) in the austenitic stainless steel precipitate due to heating.

[0074] In the case of the austenitic stainless steels shown in Table 1 and Table 2, for example, the upper limit of the heating temperature is 500°C. It becomes possible to remove as a result the non-diffusible hydrogen and the diffusible hydrogen (which are present in the austenitic stainless steel, diffuse via the mechanically-induced martensitic phase brought about by cyclic loading, and build up at crack sites that are under concentrated stress, causing thereby hydrogen embrittlement).

[0075] A thermal treatment such as the above makes it possible to remove, from the austenitic stainless steel, diffusible hydrogen and non-diffusible hydrogen that cause hydrogen embrittlement in the austenitic stainless steel, to lower thereby the hydrogen (H) content in the austenitic stainless steel down to 0.0001 wt% (1.0 wt ppm) or less. The preferred content of hydrogen (H) in the austenitic stainless steel after this thermal treatment is 0.00007 wt% (0.7 wt ppm) or less. A more preferred content of hydrogen (H) in the austenitic stainless steel after this thermal treatment is 0.00002 wt% (0.2 wt ppm) or less, and more preferably 0.000007 wt% (0.07 wt ppm) or less.

[0076] Thus, it is possible to provide an excellent austenitic stainless steel whose hydrogen content is less than in conventional austenitic stainless steels, and wherein fatigue crack growth does not accelerate even under cyclic loading involving long cycle times.

Additional experimental example 1

[0077] The experiment was performed on a thermally-treated test piece of SUS316. The test piece was a round bar 7 mm in diameter. For TDS measurement, a disc 7 mm in diameter and 0.8 mm thick was cut from the round bar. In the experiment the test piece was thermally-treated at 800°C for 20 minutes. The atmospheres during the experiment were an air atmosphere, a vacuum environment (approximately 0.006 Pa), and an Ar gas atmosphere. The thermal treatment was performed while supplying Ar gas thereto. The heating rate was 0.5°C/second up to 700°C. The escaped hydrogen was measured for heating up to 700°C.

[0078] The measurements were performed using a thermal desorption spectrometer (EMD-WA1000S/H) manufactured by ESCO, Ltd. (Musashino city, Tokyo, Japan). Fig. 12 shows the measurement results. In the graph, the horizontal axis represents the measurement temperature, and the vertical axis represents the hydrogen release intensity. The hydrogen concentration of the test piece that had not been thermally-treated was 1.5 wt ppm. The hydrogen concentration of the test piece became 0.7 wt ppm when the thermal treatment was performed in air. The hydrogen concentration of the test piece became 0.4 wt ppm when the thermal treatment was performed in a vacuum. The hydrogen concentration dropped to 0.4 wt ppm when the thermal treatment was performed under with the Ar gas flow.

Additional experimental example 2

[0079] The experiment was performed on a thermally-treated test piece of SUH660. The test piece was a round bar 7 mm in diameter. For TDS measurement, a disc 7 mm in diameter and 0.8 mm thick was cut from the round bar. For the experiment, the test piece was thermally-treated at 720°C for 16 hours. The experimental atmosphere was an air atmosphere and a vacuum environment (approximately 0.006 Pa). The hydrogen concentration of the test piece before the aging treatment was 1.3 wt ppm. The hydrogen concentration of the test piece after the aging treatment was 0.6 wt ppm.

[0080] In this manner, hydrogen content in the stainless steel could be removed by performing an aging treatment and the like during the manufacturing process of stainless steel. The heating rate for the TDS measurement was 0.33°C/second up to 700°C. The escaped hydrogen was measured for heating up to 600°C. The measurements were performed using a thermal desorption spectrometer (EMD-WA1000S/H) manufactured by ESCO, Ltd. (Musashino city, Tokyo, Japan). Fig. 13 shows the measurement results. In the graph the horizontal axis represents the measurement temperature, and the vertical axis represents the hydrogen release intensity.

Additional experimental example 3

[0081] The experiment was performed on thermally-treated test pieces of SUS304 and SUS316L. The test pieces were disc-shaped samples having a diameter of 7 mm and a thickness of 0.4 mm. The experiment atmosphere in this thermal treatment was an air atmosphere at approximately 0.1013 MPa. In the experiment, the test pieces were aged by being placed in an air atmosphere at a temperature of 300°C and 450°C, where a thermal treatment was carried out for 2 hours.

[0082] For TDS measurement there was used a disc 7 mm in diameter and 0.4 mm thick after thermal treatment. The measurements were performed using a thermal desorption spectrometer (EMD-WA1000S/H) manufactured by ESCO, Ltd. (Musashino city, Tokyo, Japan). Figs. 14A and 14B show the measurement results. In the graphs, the horizontal axis represents the measurement temperature, and the vertical axis represents the hydrogen release intensity. The heating rate for the TDS measurement was 0.5°C/second up to 700°C. In TDS, the escaped hydrogen was measured for heating up to 600°C.

[0083] Fig. 14A illustrates the measurement results of a test piece of SUS304. As the figure shows, the hydrogen concentration of the test piece before the aging treatment was 2.3 ppm. The hydrogen concentration of the test piece after the aging treatment was 0.19 ppm, in a case where the thermal treatment was performed at a temperature of 300°C, and of 0.07 ppm, in a case where the thermal treatment was performed at a temperature of 450°C.

[0084] Fig. 14B illustrates the measurement results of a test piece of SUS316L. The hydrogen concentration of the test piece before the aging treatment was 2.6 ppm. The hydrogen concentration of the test piece after the aging treatment was 0.07 ppm, in a case where the thermal treatment was performed at a temperature of 300°C, and of 0.03 ppm, in a case where the thermal treatment was performed at a temperature of 450°C.

[0085] In this manner, hydrogen content in the stainless steel was able to be removed by performing an aging treatment and the like in an air atmosphere.

INDUSTRIAL APPLICABILITY

[0086] The present invention is good for use in corrosion resistance and in fields that employ high-pressure hydrogen. More specifically, the present invention is good for use in products that have a concern of hydrogen embrittlement and delayed fracture due to hydrogen penetration, such as metal gaskets, various types of valves used in automobiles, springs, steel belts, cutting blades, fuel cells, as well as materials for valves, springs and the like ancillary to fuel cell systems. The present invention can also be used in building structures, machinery, plant and equipment.

Claims

1. An austenitic stainless steel having an austenitic phase where a crystalline structure is a face-centered cubic lattice structure,
wherein the austenitic stainless steel is subjected to a thermal treatment in an air atmosphere, at a heating temperature ranging from 200°C to 1100°C, to remove thereby diffusible hydrogen and non-diffusible hydrogen that cause hydrogen embrittlement in the austenitic stainless steel, and remove a content of hydrogen (H) in the austenitic stainless steel to 0.0001 wt% (1.0 wt ppm) or less.
2. The austenitic stainless steel according to claim 1,
wherein the diffusible hydrogen and the non-diffusible hydrogen are removed so that the hydrogen (H) is 0.00002 wt% (0.2 wt ppm) or less.
3. The austenitic stainless steel according to claim 2,
wherein the diffusible hydrogen and the non-diffusible hydrogen are removed so that the hydrogen (H) is 0.00007 wt% (0.7 wt ppm) or less.
4. The austenitic stainless steel according to claim 3,
wherein the diffusible hydrogen and the non-diffusible hydrogen are removed so that the hydrogen (H) is 0.000007 wt% (0.07 wt ppm) or less.
5. The austenitic stainless steel according to any one of claims 1 to 4,
wherein the austenitic stainless steel is heated at a heating temperature ranging from 200°C to 1100°C for 2 hours to 500 hours to remove the diffusible hydrogen and the non-diffusible hydrogen.

6. A method for removing hydrogen from an austenitic stainless steel, which is a thermal treatment method in which the austenitic stainless steel, having an austenitic phase where a crystalline structure is a face-centered cubic lattice structure, is subjected to a thermal treatment to remove hydrogen present in the austenitic stainless steel, the method comprising
5 heating the austenitic stainless steel in an air atmosphere, at a heating temperature ranging from 200°C to 1100°C, to remove thereby diffusible hydrogen and non-diffusible hydrogen in the austenitic stainless steel, to a content of 0.0001 wt% (1.0 wt ppm) or less.
7. The method for removing hydrogen from an austenitic stainless steel according to claim 6,
10 wherein there are removed the diffusible hydrogen and the non-diffusible hydrogen that are present in the austenitic stainless steel, diffuse via a mechanically-induced martensitic phase brought about by cyclic loading, accumulate in cracks that are under stress concentration, and cause hydrogen embrittlement in the austenitic stainless steel.
8. The method for removing hydrogen from an austenitic stainless steel according to claim 6,
15 wherein the austenitic stainless steel is held, from 2 hours to 500 hours at a temperature lower than a sensitization temperature at which chromium (Cr) carbides in the austenitic stainless steel precipitate due to heating, and there are removed the diffusible hydrogen and the non-diffusible hydrogen that cause hydrogen embrittlement in the austenitic stainless steel.
9. The method for removing hydrogen from an austenitic stainless steel according to claim 7 or 8,
20 wherein the hydrogen (H) content in the austenitic stainless steel is 0.00007 wt% (0.7 wt ppm) or less.
10. The method for removing hydrogen from an austenitic stainless steel according to claim 9,
25 wherein the hydrogen (H) content in the austenitic stainless steel is 0.00002 wt% (0.2 wt ppm) or less.
11. The method for removing hydrogen from an austenitic stainless steel according to claim 10,
wherein the hydrogen (H) content in the austenitic stainless steel is 0.000007 wt% (0.07 wt ppm) or less.
12. The method for removing hydrogen from an austenitic stainless steel according to claim 6,
30 wherein the diffusible hydrogen and the non-diffusible hydrogen diffuse via a mechanically-induced martensitic phase brought about by cyclic loading at low-frequency, accumulate in cracks that are under stress concentration, increase thereby the growth rate of fatigue cracks, and cause hydrogen embrittlement in the austenitic stainless steel.

Fig. 1A

Fatigue test piece

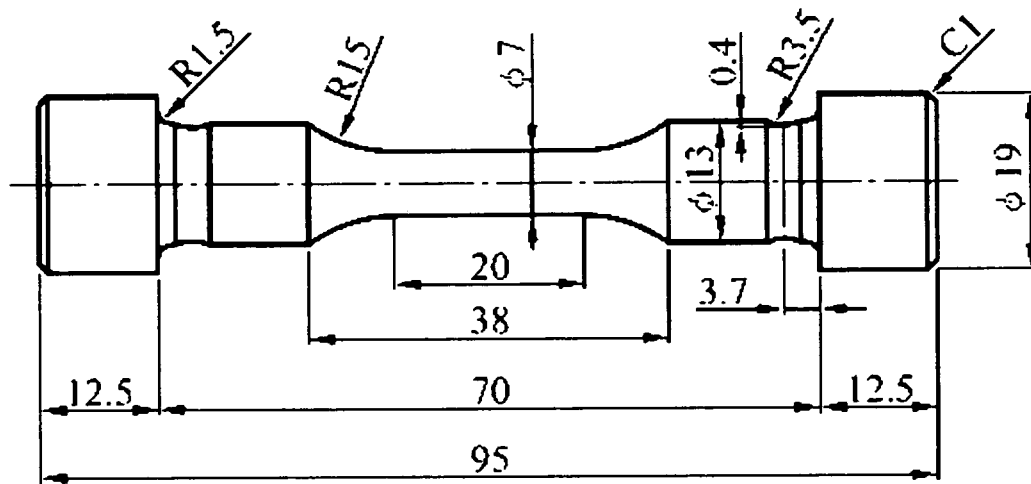


Fig. 1B

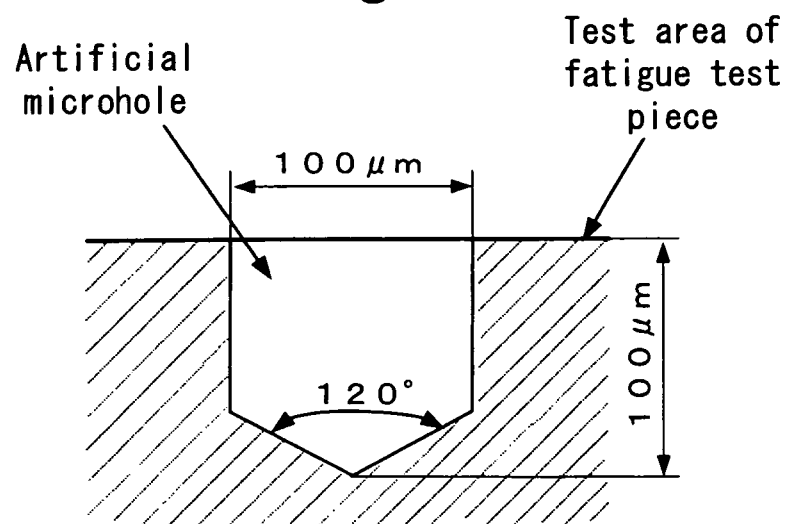


Fig. 2

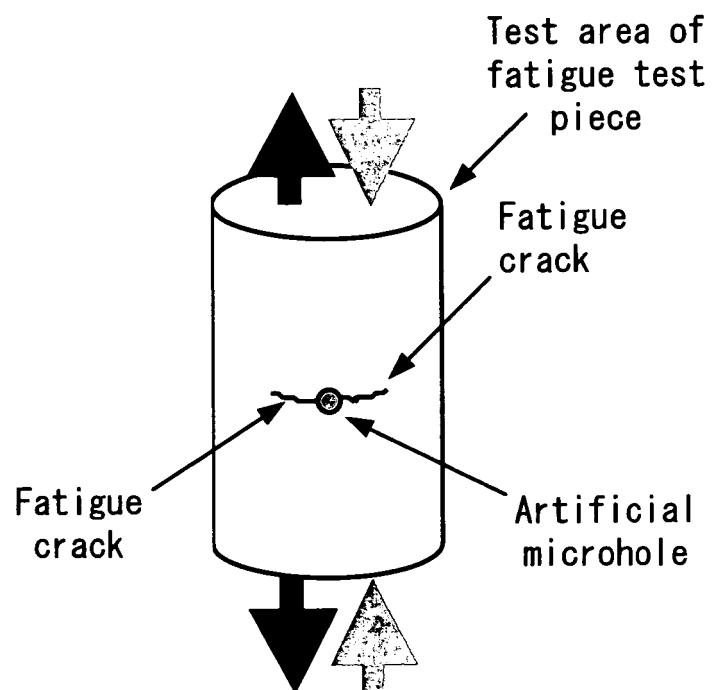


Fig. 3

Procedure for application of prestrain
in fatigue test piece

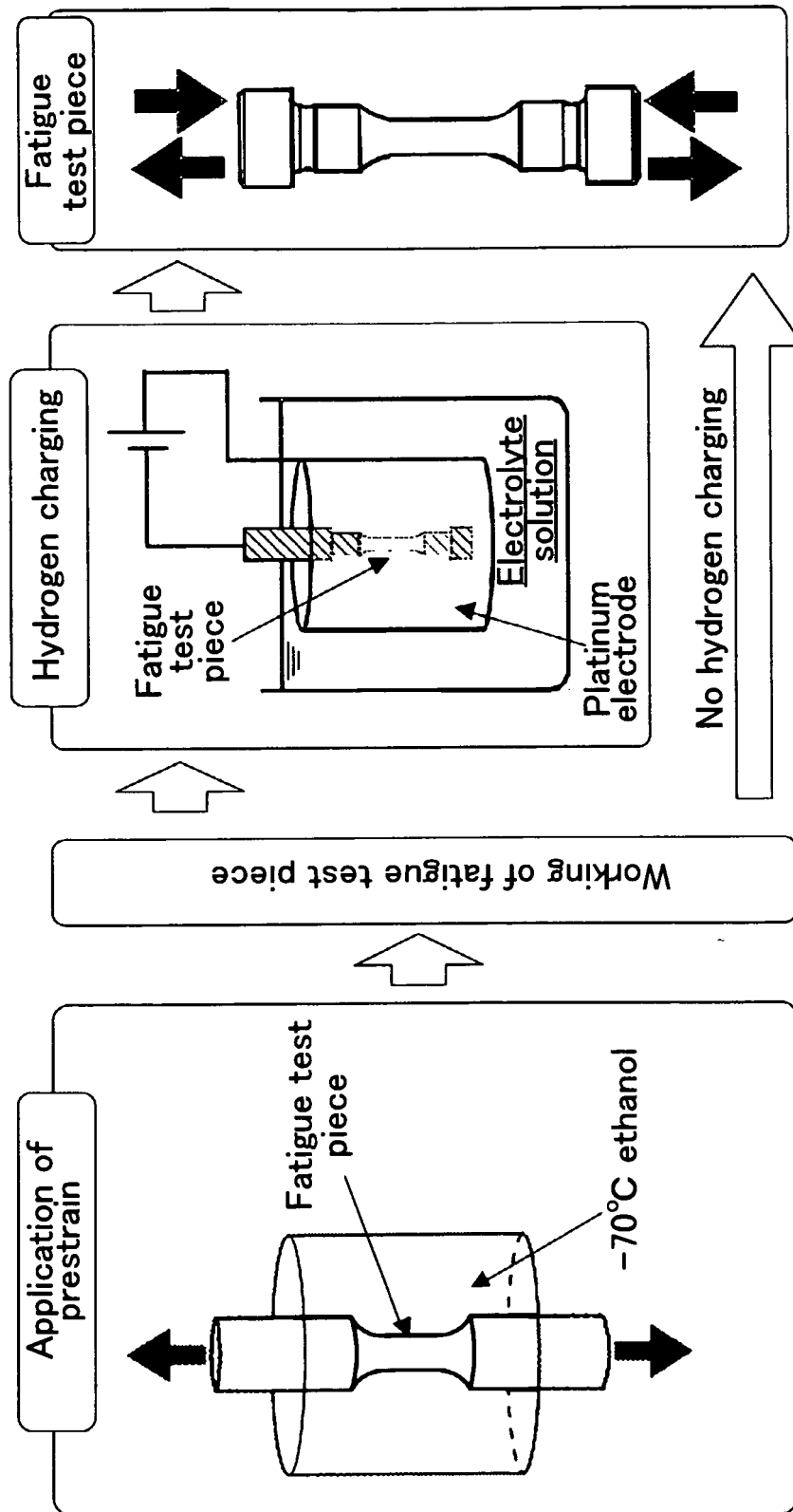


Fig. 4



Fig. 5A

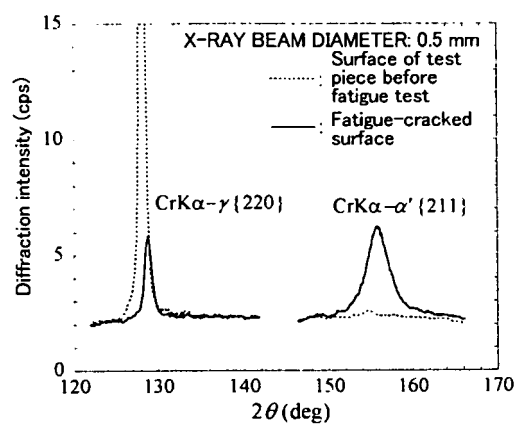
SUS304 ($\sigma = 240$ MPa, $b = 0.35$ mm)

Fig. 5B

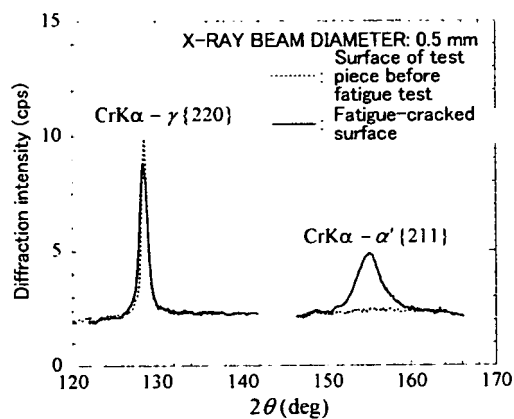
SUS316 ($\sigma = 240$ MPa, $b = 0.35$ mm)

Fig. 5C

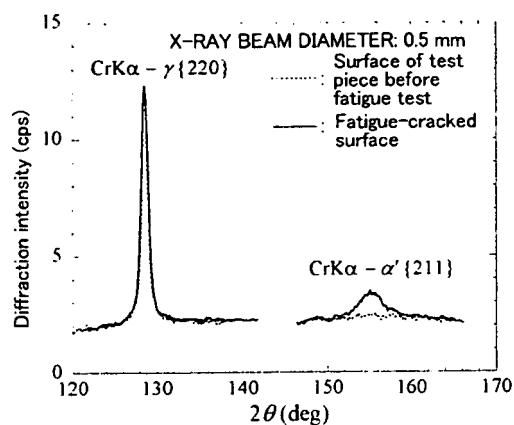
SUS316L ($\sigma = 260$ MPa, $b = 0.35$ mm)

Fig. 6A

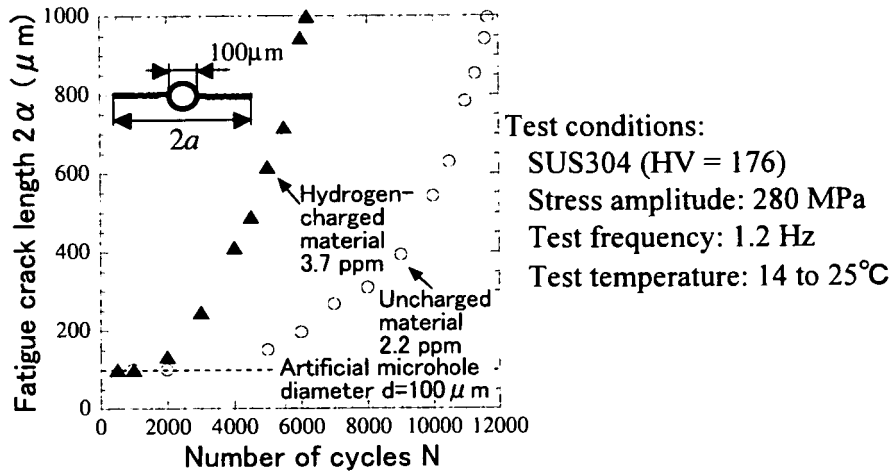


Fig. 6B

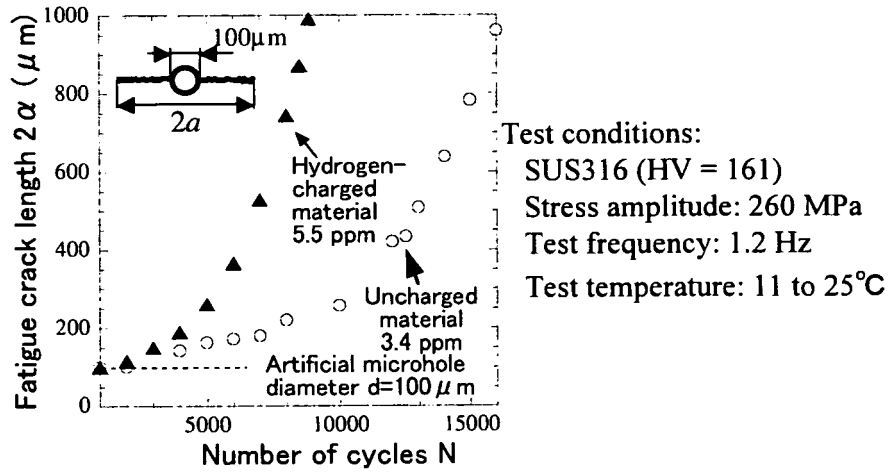


Fig. 6C

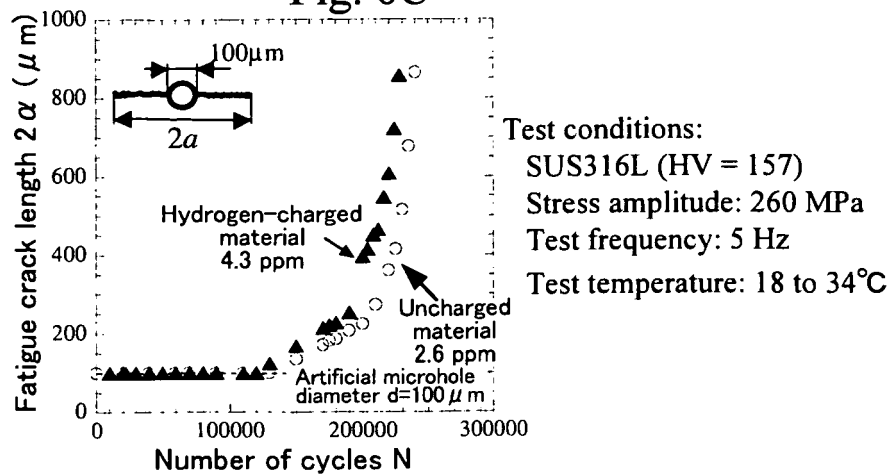


Fig. 7

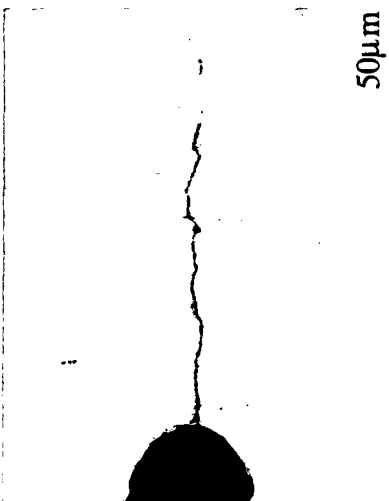
	SUS304($\sigma=280\text{MPa}$, $f=1.2\text{ Hz}$)	SUS316($\sigma=260\text{MPa}$, $f=1.2\text{ Hz}$)	SUS316L($\sigma=260\text{MPa}$, $f=5\text{ Hz}$)
Uncharged material	 $N = 1.1 \times 10^4$, $2a = 782\text{ }\mu\text{m}$, 2.2ppm	 $N = 1.4 \times 10^4$, $2a = 638\text{ }\mu\text{m}$, 3.4ppm	 $N = 2.35 \times 10^5$, $2a = 677\text{ }\mu\text{m}$, 2.6ppm
Hydrogen-charged material	 $N = 5.2 \times 10^3$, $2a = 801\text{ }\mu\text{m}$, 3.7ppm	 $N = 7.0 \times 10^3$, $2a = 528\text{ }\mu\text{m}$, 5.5ppm	 $N = 2.24 \times 10^5$, $2a = 721\text{ }\mu\text{m}$, 4.3ppm

Fig. 8

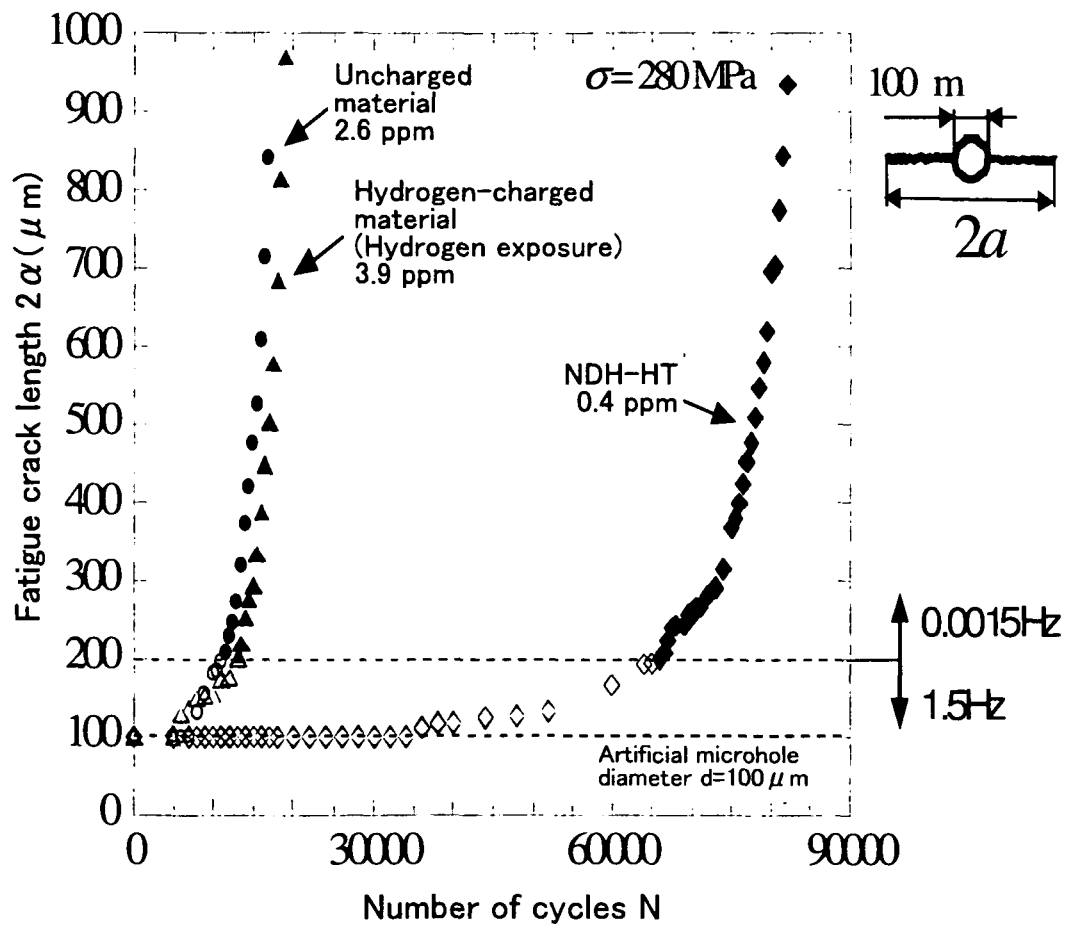


Fig. 9

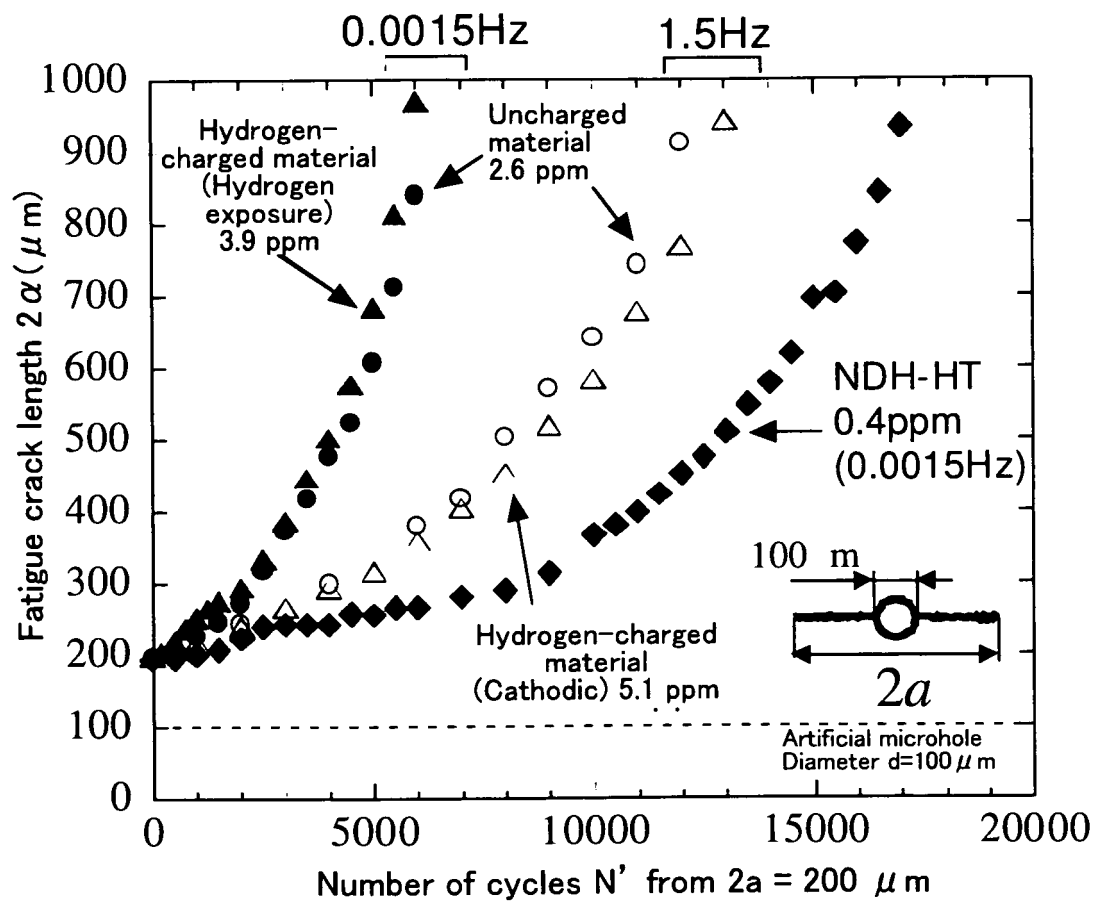


Fig. 10

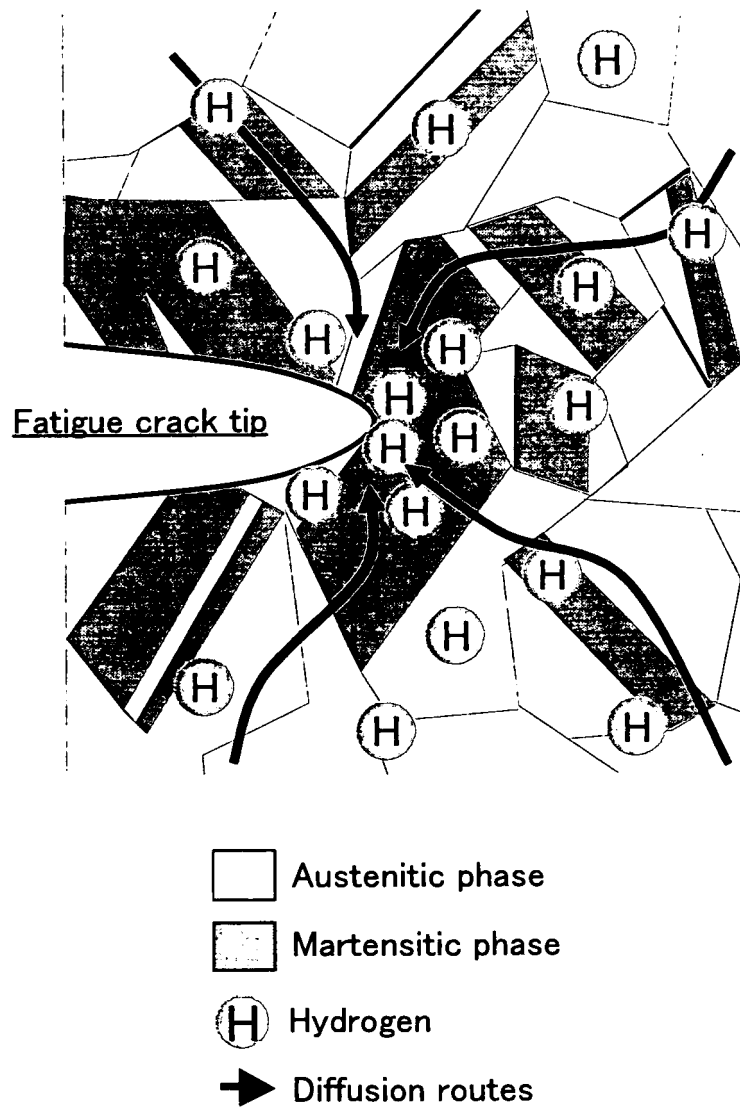


Fig. 11A

Face centered cubic lattice
(FCC)

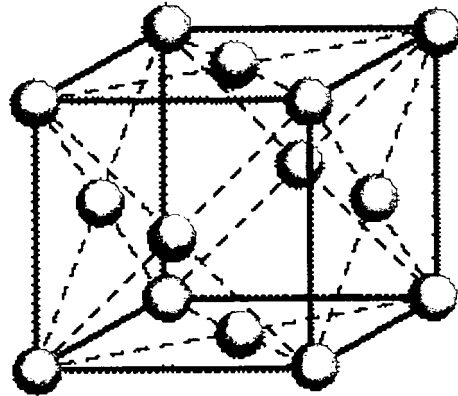


Fig. 11B

Body centered cubic lattice
(BCC)

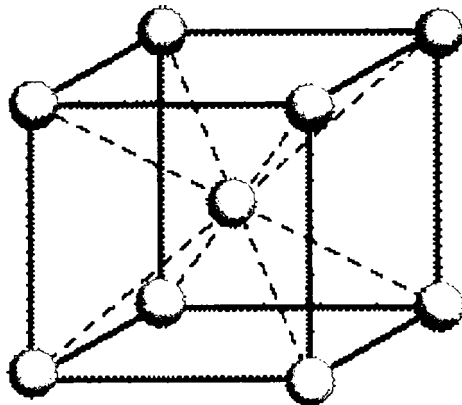


Fig. 12

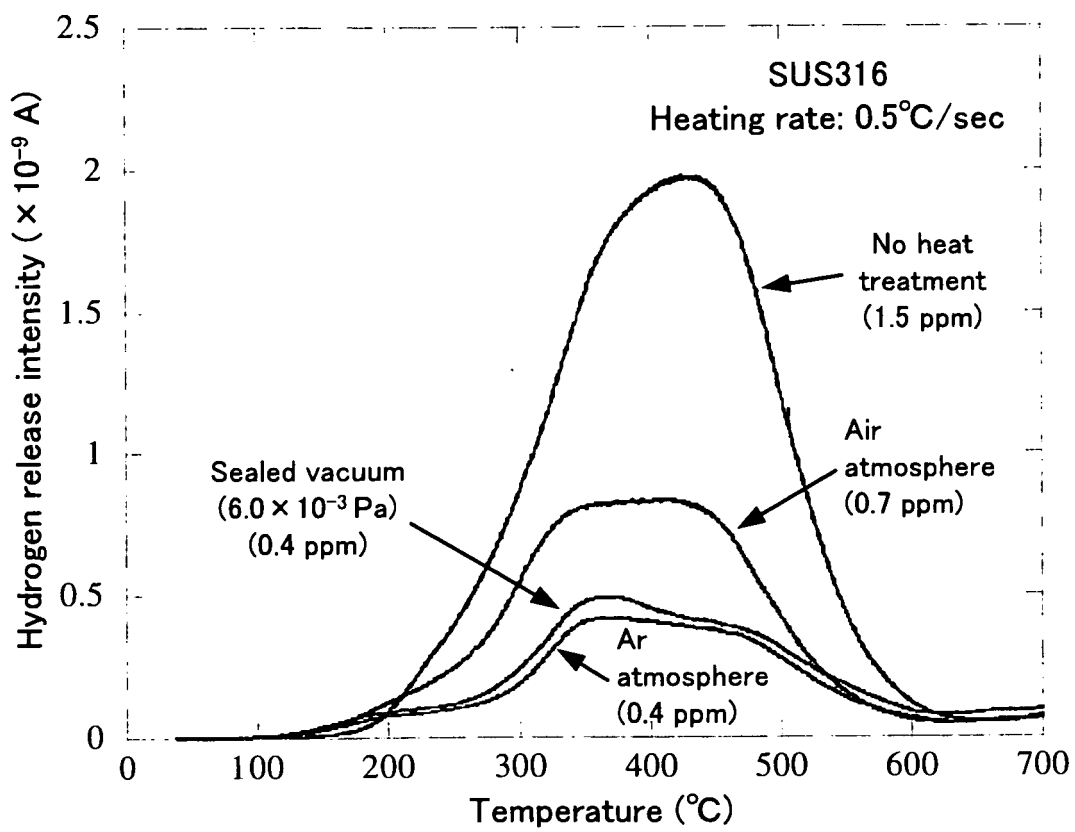


Fig. 13

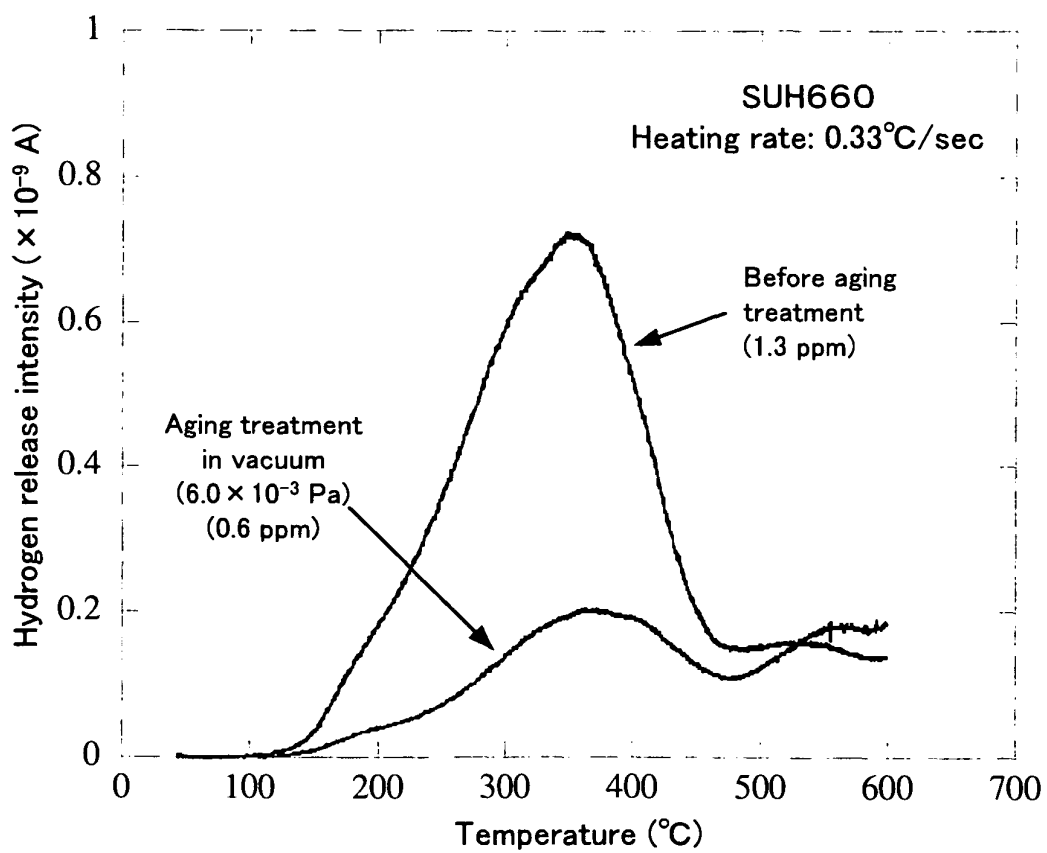


Fig. 14A

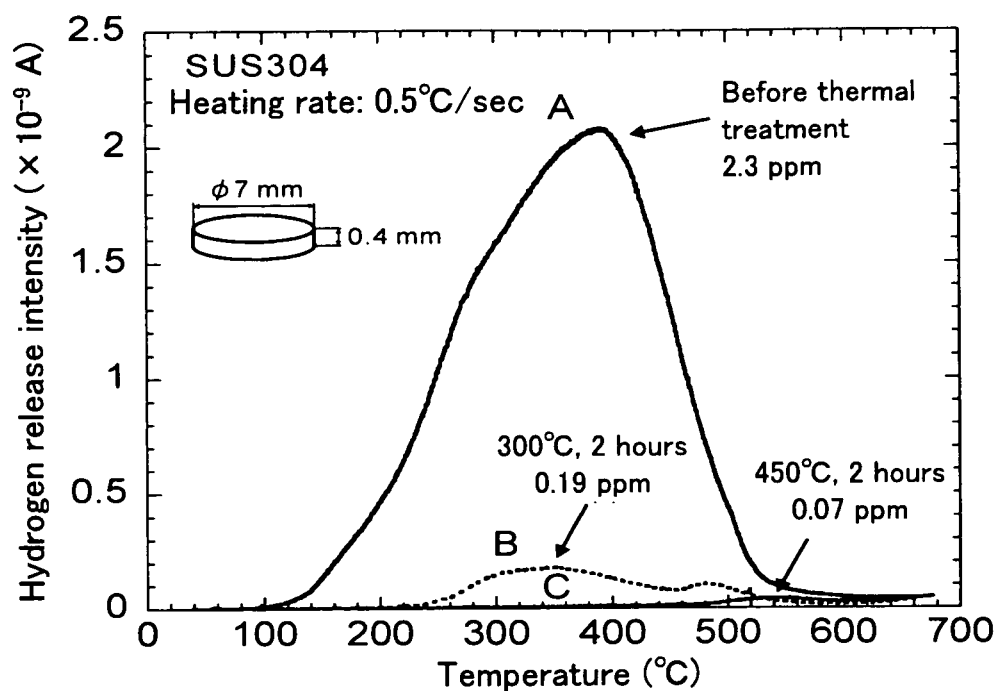


Fig. 14B

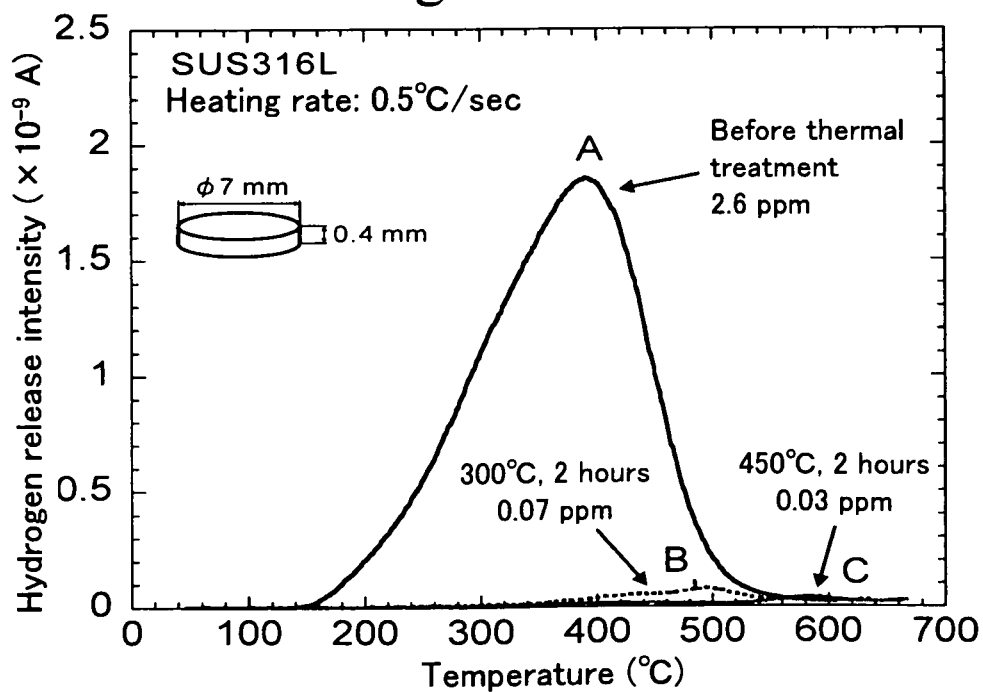
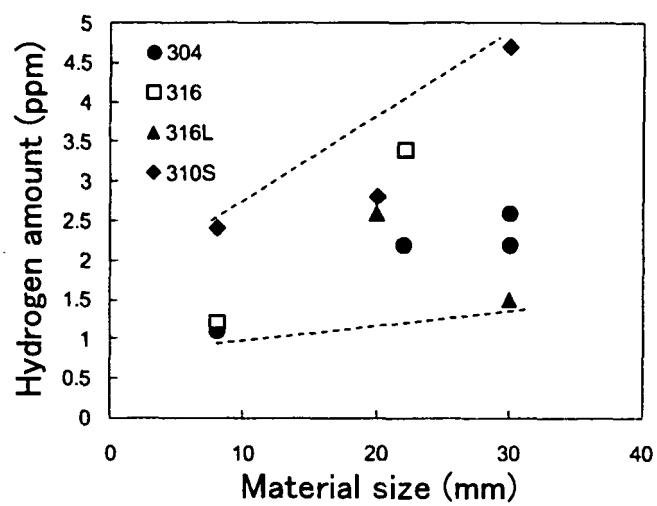


Fig. 15



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2009/052131

A. CLASSIFICATION OF SUBJECT MATTER

C21D6/00(2006.01)i, C21D3/06(2006.01)i, C22C38/00(2006.01)i, C22C38/58(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C21D6/00, C21D3/06, C22C38/00-38/60

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

JSTPlus (JDreamII)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	JP 2002-146483 A (Nippon Steel Corp., Nippon Seisen Co., Ltd.), 22 May, 2002 (22.05.02), Par. Nos. [0018], [0026], [0035]; tables 1, 4 (Family: none)	1-7, 9-12 8
X Y	JP 10-121208 A (Nippon Steel Corp.), 12 May, 1998 (12.05.98), Par. Nos. [0010], [0015]; tables 1, 2 (Family: none)	1-7, 9-12 8
Y	Shigeo OWAKU, Kinzoku Netsushori Yogo Jiten -revised edition-, The Nikkan Kogyo Shinbun, Ltd., 30 October, 1985 (30.10.85), page 13, lines 5 to 9	8

☒ Further documents are listed in the continuation of Box C.
 ☐ See patent family annex.

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"A" document defining the general state of the art which is not considered to be of particular relevance

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"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

"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

"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

"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

"&" document member of the same patent family

Date of the actual completion of the international search
07 May, 2009 (07.05.09)Date of mailing of the international search report
19 May, 2009 (19.05.09)Name and mailing address of the ISA/
Japanese Patent Office

Authorized officer

Facsimile No.

Telephone No.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2009/052131

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 11-181517 A (Nippon Steel Corp.), 06 July, 1999 (06.07.99), Par. No. [0006] (Family: none)	1-12
A	JP 2005-298932 A (Nippon Steel & Sumikin Stainless Steel Corp.), 27 October, 2005 (27.10.05), Par. Nos. [0050] to [0052]; tables 1, 4 (Family: none)	1-12
P, X	JP 2008-208451 A (National Institute of Advanced Industrial Science and Technology, Kyushu University), 11 September, 2008 (11.09.08), Full text; all drawings & WO 2008/093453 A1 & CA 2649355 A1	1-12

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REFERENCES CITED IN THE DESCRIPTION

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- JP H10121208 B [0010]
- JP 2005298932 A [0010]

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- **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 [0010]