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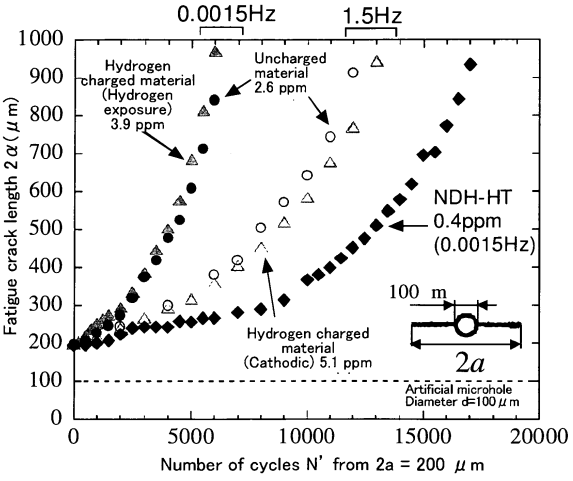
(54) AUSTENITE BASED STAINLESS STEEL AND METHOD OF DEHYDROGENATING THE SAME

(57) By focusing on the non-diffusible hydrogen that causes hydrogen embrittlement of austenitic stainless steel, the present invention provides an austenitic stainless steel in which the non-diffusible hydrogen is removed by maintaining the austenitic stainless steel in a vacuum of 0.2 Pa or less and heating at a heating temperature of 200°C to 500°C for 460 hours or less to remove the hydrogen (H) contained therein to a level of 0.00007 mass% (0.7 mass ppm) or less.

Fig.9



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Description

TECHNICAL FIELD

[0001] The present invention concerns an austenitic stainless steel with reduced hydrogen embrittlement and a process for removing hydrogen therefrom. More specifically, the present invention concerns an austenitic stainless steel wherein the effect of hydrogen present therein on the growth of fatigue cracks occurring therein is reduced, and a process for removing hydrogen therefrom.

BACKGROUND

[0002] From the standpoint of global environmental concerns, the use of hydrogen as a next generation energy source has received considerable attention, and R&D on this topic is quite active. Particularly, one important subject that has received emphasis is the development and practical application of stationary fuel cells, fuel cell-powered vehicles, etc., that utilize hydrogen as fuel. The use of stainless steel as a material for high pressure hydrogen tanks and parts thereof, piping, and the like in this fuel cell system has already been investigated (for example, see patent document 1).

[0003] The components of typical austenitic stainless steel are shown in Table 1. The first column in this Table 1 lists the names of stainless steels and the heat-resistant steels as defined in the Japanese Industrial Standards (JIS). The last column of Table 1 shows the Vickers hardness of the stainless steel (hereinafter, HV). Other columns are the chemical compositions of the stainless steel, and the amounts of the components are expressed in units of mass%. However, the content of hydrogen (H) is expressed as mass ppm (parts per million by mass).

[0004]

[Table 1](Units: mass%, *ppm by mass)

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

[0005] It is known that hydrogen diffuses through metallic materials and decreases both the static strength and fatigue strength thereof (non-patent documents 1 and 2). Various processes for removing this hydrogen and methods for predicting the effect of hydrogen have been proposed. In patent document 2, for example, after the plating process austenitic stainless steel is heat-treated by maintaining it 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 the hydrogen embrittlement of austenitic stainless steel is predicted and judged based on the chemical composition thereof.

[0006] Non-patent document 1 presents fatigue testing results for austenitic stainless steels in compliance with SUS304, SUS316, and SUS316L. This fatigue testing was conducted by comparing these austenitic stainless steels with their hydrogen-charged counterparts. The fatigue crack growth rate of hydrogen-charged SUS304 and SUS316 was faster than in the corresponding uncharged steels. However, no clear difference was seen with SUS316L.

[0007] In addition, non-patent document 1 presents fatigue test results for JIS SUS304 and the SUS316L austenitic stainless steels after the test piece was prestrained and a microhole of about 100 μm was formed therein. The fatigue crack growth rate was accelerated ten-fold in hydrogen-charged SUS304 compared with the uncharged steel counterpart. Likewise, the fatigue crack growth rate was accelerated two-fold in SUS316L.

[0008] However, even semi-stable austenitic stainless steel can undergo stress-induced martensitic transformation due to cold-working and cyclic stress. Persons skilled in the art in this industry, including groups of researchers in academic societies, have commonly believed that hydrogen had almost no effect on the fatigue crack growth rate in the austenitic stainless steels such as JIS SUS316L. Non-patent document 1 presents results that reverse this common belief, and because these results were obtained by applying cyclic loading at a low frequency of 5Hz or less, this finding is very significant.

[0009] In other words, it has been verified that the growth rate of fatigue cracks is accelerated by low-frequency cyclic loading in austenitic stainless steel such as SUS316L. On the other hand, 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 (see page 130)."

[0010]

[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 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 (November 4 to 6, 2005, Fukuoka) P86 p. 595-596.
[Non-patent document 2] Toshihiko KANEZAKI, Chihiro NARAZAKI, Yoji MINE, Saburo MATSUOKA, and Yukitaka MURAKAMI: Effect of hydrogen on fatigue crack growth and martensitic transformation of stainless steels. Transactions of the Japan Society of Mechanical Engineers A. Vol. 72, No. 723, (November 2006), p. 123-130. (manuscript received: May 1, 2006)

[0011] At present, however, sufficient analysis has not been performed concerning 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 involving how diffusible hydrogen and non-diffusible hydrogen influence changes in the amount of martensitic transformation, the effect of acceleration in the hydrogen diffusion rate, and the fatigue crack growth rate in a material have not been sufficiently clarified.

[0012] Furthermore, when stainless steel is used for equipment and apparatuses related to hydrogen fuel utilization, it is exposed to a variety of environmental influences depending on the usage environment. For example, when stainless steel is used for the high pressure hydrogen container, piping, and the like in a fuel cell-powered vehicle, loading and release are repeated in a relatively slow cycle that involves 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. In other words, it was thought that a fatigue test using a load with a long cycle could be replaced by a fatigue test with a quick repetition rate.

[0013] Moreover, low frequency cyclic loading occurs due to temperature variations in the outside air temperature and the like. An example of cyclic loading due to variations in the outside air temperature is 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 gradient 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 at fuel cell vehicle-related facilities, facilities for supplying fuel for fuel cells, and the like will have a cycle measured in single day units as noted above, and the hydrogen fill time will be long. In addition, a fuel cell-powered vehicle is dependent on the environment in which it operates, and it will have a temperature gradient cycle ranging from a few degrees to several tens of degrees centigrade, and a time cycle expressed in units ranging from subseconds to several hours.

DISCLOSURE OF THE INVENTION

[0014] The present invention is based on the above technological background, and it attains the following objects.
An object of the present invention is to provide an austenitic stainless steel for reducing the effect of hydrogen on the growth rate of fatigue cracks that occur in austenitic stainless steel, and a process for removing the hydrogen therefrom.
[0015] Another object of the present invention is to focus on both diffusible hydrogen and non-diffusible hydrogen that cause hydrogen embrittlement in austenitic stainless steel and provide an austenitic stainless steel having both removed therefrom, and to provide a process for removing the hydrogen therefrom.
[0016] Another object of the present invention is to focus on the diffusible hydrogen and the non-diffusible hydrogen that become a problem with cyclic loading having a long cycle time and provide an austenitic stainless steel having both removed therefrom, and to provide a process for removing the hydrogen therefrom.
[0017] Another object of the present invention is to provide an austenitic stainless steel wherein the diffusible hydrogen and non-diffusible hydrogen present in austenitic stainless steel are removed therefrom during a manufacturing step thereof, and a process for removing the hydrogen therefrom.

Definition of terms

[0018] The present invention uses the following technical terms in the meanings defined below. Hydrogen charge means causing hydrogen to permeate the material. Hydrogen charge method refers to a method whereby the material is exposed in a high pressure hydrogen chamber, a method wherein cathodic charging is performed, and a method wherein 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 the material during the manufacturing process or cracks from holes and the like that are artificially introduced into the material as a result of cyclic loading.
[0019] Fatigue crack growth rate means the rate at which the fatigue crack progresses. Austenitic stainless steel refers to Cr-Ni series steel wherein chromium and nickel are added to iron to produce a stainless steel in the austenitic phase with increased corrosion resistance in corrosive environments and the like. Table 1 shows a list of this kind of stainless steel. The austenitic phase is a phase of iron at a temperature range of 911 to 1392°C in 100% pure iron (Fe), and it has a face centered cubic lattice structure (hereinafter, FCC lattice structure).
[0020] The FCC lattice is shown in Figure 11(a). The austenitic phase can also exist at room temperature when alloying elements such as chromium and nickel are added to iron. The martensitic phase is a conformation obtained by quenching steel at a high-temperature, stable austenitic phase, and it has a body centered cubic lattice structure (hereinafter, BCC lattice structure). The BCC lattice is shown in Figure 11(b). Moreover, the martensitic phase is caused by adding stress such as cold-working and the like to austenitic phase stainless steel at ordinary ambient temperatures.
[0021] This transformation from an austenitic phase with an FCC structure to a martensitic phase with a BCC structure by cold working is called stress-induced martensitic transformation. Diffusible hydrogen refers to hydrogen that is present in the material and exits the material over time at room temperature. This diffusible hydrogen causes the hydrogen embrittlement of the material. Hydrogen that cannot exit the material over time even at temperatures from room temperature to about 200°C, is called non-diffusible hydrogen.
[0022] The present invention adopts the following means to achieve the aforementioned objects.
The inventors of the present invention ascertained the fact that non-diffusible hydrogen in an austenitic stainless steel is related to fatigue crack growth.
The present invention concerns an austenitic stainless steel having an austenitic phase in which the crystal structure is an FCC lattice structure and a process for removing the hydrogen therefrom. The present invention is one wherein the diffusible hydrogen and the non-diffusible hydrogen that cause hydrogen embrittlement of austenitic stainless steel are removed, with the hydrogen (H) contained in the austenitic stainless steel being removed to a level of 0.00007 mass% (0.7 mass ppm) or less.
[0023] A heat treatment at a heating temperature of 200°C or higher is preferred for the removal of diffusible hydrogen and non-diffusible hydrogen from austenitic stainless steel. Moreover, the upper limit of the heating temperature for the heat treatment at this time is preferably no more than 500°C. It is preferred that the heat treatment to remove the diffusible hydrogen and non-diffusible hydrogen is performed under vacuum.
[0024] Moreover, the temperature range for the heating temperature is 200 to 500°C, and this range is preferred for removing both the non-diffusible hydrogen and the diffusible hydrogen, which are present in austenitic stainless steel, diffuse via the stress-induced martensitic phase brought about by cyclic loading, concentrate in the cracks undergoing concentrated stress, and cause hydrogen embrittlement therein, to thereby remove the hydrogen (H) contained therein to the aforementioned amount.

[0025] It is preferred that the heating temperature is a temperature lower than the sensitization temperature, which is the temperature at which chromium (Cr) carbide in austenitic stainless steel precipitates due to the heat. Moreover, it is preferred that the aforementioned vacuum atmosphere is an environment of 0.2 Pa or less. In addition, it is preferred that the heat treatment is performed by maintaining the heating temperature in the aforementioned vacuum atmosphere for 460 hours or less.

[0026] The amount of hydrogen (H) contained in the austenitic stainless steel after removing the diffusible hydrogen and the non-diffusible hydrogen is preferably 0.00004 mass% (0.4 mass ppm) or less. Furthermore, the amount of hydrogen (H) contained in the austenitic stainless steel after removing the diffusible hydrogen and the non-diffusible hydrogen is more preferably 0.00001 mass% (0.1 mass ppm) or less.

[0027] It is preferable that the heat treatment is performed for the predetermined time in the process of manufacturing the austenitic stainless steel, and the hydrogen is removed to adjust the hydrogen (H) to 0.00007 mass% (0.7 mass ppm) or less. At that time, the heat treatment temperature is preferably 200°C or more, and less than the melting point temperature of the stainless steel. The heating time for this purpose preferably ranges from 30 seconds or more to several tens of hours or less. An inert gas flow atmosphere is preferred for this process. The manufacturing steps for austenitic stainless steel are the ones used when manufacturing stainless steel, and they include the steps of a solution heat treatment and an aging treatment.

[0028] The hydrogen removal treatment in the manufacturing process can be performed in a vacuum or an atmosphere wherein the hydrogen partial pressure is low, e.g., an inert gas atmosphere. Moreover, the heat treatment preferably lasts from a few minutes to several tens of hours long.
In the case of a solution heat treatment, the most preferred temperature for the heat treatment is 920°C or higher.
In the case of an aging treatment, the most preferred temperature for the heat treatment is 700°C or higher.
In addition, it is preferred that the austenitic stainless steel is one of the aforementioned austenitic stainless steels or heat resistant austenitic steels shown in Table 1.

[0029] The present invention provides the following advantageous effect. In the present invention austenitic stainless steel is heat-treated at a temperature of 200°C or higher to remove the non-diffusible hydrogen and the diffusible hydrogen, thereby making it possible to provide an austenitic stainless steel that is highly resistant to fatigue crack growth.

BRIEF DESCRIPTION OF THE DRAWINGS

[0030]

Figure 1 is a line drawing showing the fatigue test piece, Figure 1(a) is a drawing showing the shape of the fatigue test piece, and Figure 1(b) is a drawing showing the shape of the artificial microhole formed in the fatigue test piece;
Figure 2 shows a line drawing of the test area in the fatigue test piece and the fatigue crack starting at the small artificial hole and progressing therefrom;
Figure 3 is a schematic diagram of the procedure for applying the prestrain to the fatigue test piece;
Figure 4 is a photograph of the fatigue cracks emanating from the artificial microhole after fatigue testing;
Figure 5 shows 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 Figure 5(a) shows the measurement results for SUS304, Figure 5(b) shows the measurement results for SUS316, and Figure 5(c) shows the measurement results for SUS316L;
Figure 6 is a graph showing the relationship between the length of the cracks caused by fatigue testing and number of cycles wherein Figure 6(a) shows the results for SUS304, Figure 6(b) for SUS316, and Figure 6(c) for SUS316L;
Figure 7 shows photographs of fatigue cracks in SUS304, SUS316, and SUS316L observed by the replica method;
Figure 8 is a graph showing the results of fatigue testing of SUS316L;
Figure 9 is a graph showing the result of the fatigue testing of SUS316L;
Figure 10 is a conceptual drawing showing the circumstances wherein the diffusible hydrogen and the non-diffusible hydrogen diffuse through the transformed martensitic phase;
Figure 11 is a schematic drawing showing the lattices of the crystal structures of the austenitic phase and martensitic phase wherein Figure 11(a) shows the face centered cubic lattice structure (FCC) of the austenitic phase, and Figure 11(b) shows the body centered cubic lattice structure (BCC) of the martensitic phase;
Figure 12 is a graph showing the results of Additional Experimental Example 1; and
Figure 13 is a graph showing the results of Additional Experimental Example 2.

BEST MODE FOR CARRYING OUT THE INVENTION

[0031] Below the mode of the present invention is explained through examples. First of all, the way hydrogen affects the growth rate of fatigue cracks in austenitic stainless steel will be explained. After a conventional heat treatment (solution heat treatment) is performed, austenitic stainless steels such as SUS304, SUS316, and SUS316L shown in Table 1 contain 1 to 4.7 mass ppm of non-diffusible hydrogen. In the past persons skilled in the art believed that this non-diffusible hydrogen had no effect on hydrogen embrittlement.

[0032] However, the fatigue tests described below have determined that non-diffusible hydrogen affects hydrogen embrittlement. Hydrogen embrittlement resulting from non-diffusible hydrogen has been verified at a low frequency fatigue testing speed of about 0.0015 Hz in (approximately 11 minutes as the repetition time of one cycle) in particular. The inventors of the present invention performed the following tests and observed how non-diffusible hydrogen affected the growth rate of the fatigue cracks. One example of such testing is shown herein.

Test piece

[0033] The materials used were the SUS304, SUS316, and SUS316L(A) (hereinafter, simply called SUS316L) austenitic stainless steels shown in Table 1. A solution heat treatment was performed on the SUS304, SUS316, and SUS316L steels used. The shape of the fatigue test piece is shown in Figure 1(a). The surface of the test piece was finished by buffing after polishing with # 2000 emery paper.

[0034] As shown in Figure 1(b), 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 inserted in the center of the test area of the test piece. The test area was a cylindrical part at the center of the test piece, and the length of the cylinder was approximately 20 mm. The top and bottom surfaces of the cylinder were mutually parallel, and lay perpendicular to the lengthwise axis of the test piece. Figure 2 illustrates an outline of the test piece and the shape of the inserted artificial microhole. In the case of a hydrogen-charged fatigue test piece, the piece buffed immediately after the end of hydrogen charging and the artificial microhole was drilled.

X-ray diffraction

[0035] The amount of the martensite in the test area of the fatigue test piece of austenitic stainless steel was measured by x-ray diffraction. The x-ray diffraction was performed using a miniature x-ray stress measurement apparatus PSPC-RSF/KM manufactured by Rigaku Corporation (Akishima, Tokyo). 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 CrK α-rays. In SUS304, SUS316, and SUS316L the content of martensite in the test area before fatigue testing was about 3%.

[0036] The content of martensite in the hydrogen-charged test areas was also about 3%. The content of martensite was measured in two places before the artificial microhole was inserted. 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

[0037] Hydrogen charging was performed using the cathodic charging method. The hydrogen charging conditions were an aqueous sulfuric acid solution at pH = 3.5, platinum anode, and current density i = 27 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

[0038] To investigate the relationship between the acceleration in fatigue crack growth rate resulting from hydrogen and the amount of martensitic transformation, prestraining was performed on SUS304 and SUS316L, and martensite-transformed test pieces therefrom were used. Figure 3 shows a chart illustrating the prestraining procedure. Because prestraining promotes martensitic transformation, it was performed in -70°C ethanol. After prestraining, the test piece was worked into the shape shown Figure 1(a). For the SUS304, prestraining was applied at a plastic strain (true strain) of $\varepsilon_p = 0.28$, and for SUS316L prestraining was applied at a plastic strain of $\varepsilon_p = 0.35$.

[0039] When the Vickers hardness was measured after the prestrain was applied (measurement load of 9.8 N), it was HV = 426 (10 point average) for SUS304, and HV = 351 (10 point average) for SUS316L. The variation was within ±4%. After the test piece was polished, the amount of martensite in the test area after prestraining was measured by x-ray diffraction. The martensite content in SUS304 was 65% to 69% by specific volume, and in SUS316L was 26% to 28% by specific volume. The amount of martensite was measured at two locations 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.

Fatigue test method

[0040] 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 repetition rate of 0.0015 to 5 Hz, and a stress ratio of $R = -1$. The repetition rate was adjusted so that the surface temperature of the test area did not exceed 60°C during the fatigue test. The fatigue cracks were observed using the replica method, and the length of the fatigue cracks measured.

[0041] Observation of the fatigue cracks by the replica method revealed the following. After a 0.034 mm thick acetyl cellulose film (hereinafter, called the replica film) had been immersed in methyl acetate liquid for a short time, it was applied to observation site. Two or three minutes elapsed after the replica film was applied, and the replica film was then peel off after it had dried. Gold was deposited on the recovered replica film, and the fatigue cracks in the test area were observed with a metallurgical microscope.

[0042] Therefore, even if the test piece was not observed directly, the location of a target fatigue crack could be observed. In the case of hydrogen-charged material, a sample 7 mm in diameter and 0.8 mm in thickness was cut out from the test area immediately after the end of fatigue testing, maintained in a vacuum chamber, and heated at a constant heating rate. The vacuum chamber internal pressure was 1×10^{-7} Pa 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°C/sec.

[0043] Heating the sample in the vacuum chamber caused hydrogen to escape therefrom, and the amount of escaped hydrogen was measured with a quadrupole mass analyzer type thermal desorption spectrometer (hereinafter, called TDS). The TDS used for measurement was a thermal desorption spectrometer model EMD-WA1000S/H manufactured by ESCO, Ltd. (Musashino, Tokyo). The precision of the TDS measurement was 0.01 mass ppm.

Measured properties

[0044] Figure 4 is a photograph of fatigue cracks that developed from the artificial microhole drilled in hydrogen-charged SUS304 after fatigue testing. From the photo it can be confirmed that the fatigue cracks spread from the artificial microhole. These fatigue cracks developed bilaterally from the artificial microhole, and it is clear that they grew in a roughly symmetrical manner.

[0045] Figure 5 shows 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 line in Figure 5 shows the results of measuring the surface of the test area before fatigue testing. The solid line shows the results of measuring fatigue cracked surface after fatigue testing. Figure 5(a) shows the measurement results for SUS304, and from this measurement it is clear that after the fatigue testing the austenitic phase has decreased and the martensitic phrase has increased compared with before the fatigue testing.

[0046] Figure 5(b) shows the measurement results for SUS316, and from this measurement it is clear that after fatigue testing the austenitic phase has decreased a little and the martensitic phrase has increased compared with before fatigue testing. Figure 5(c) shows the measurement results for SUS316L, and from this measurement it is clear that after fatigue testing the martensitic phrase has increased compared with before fatigue testing. Almost no change in the austenitic phase was seen for SUS316L.

[0047] Figure 6 is a graph showing the relationship between the length of the cracks caused by fatigue testing and number of cycles. Figure 6(a) shows the results for SUS304, Figure 6(b) for SUS316, and Figure 6(c) for SUS316L. For each material (SUS304, SUS316, and SUS316L) the measurement results are shown for hydrogen-charged pieces and uncharged pieces. The repetition rate was 1.2 Hz for SUS304 and SUS316, and 5 Hz for SUS316L.

[0048] From this graph it is clear that the crack growth rate is accelerated in hydrogen-charged SUS304 and SUS316 compared with the uncharged material. For example, in hydrogen-charged material the number of cycles N until crack length $2a$ reaches 400 μm is lower than in uncharged material. In these cases, the fatigue crack growth rate is approximately twice as fast in the hydrogen-charged pieces. On the other hand, for SUS316L the fatigue crack growth rate is slightly higher in the hydrogen-charged material than in the uncharged material, but no clear difference is seen.

[0049] Figure 7 shows photographs of fatigue cracks in SUS304, SUS316, and SUS316L observed by the replica method. As can be seen in the photograph in Figure 4, the fatigue cracks essentially grow symmetrically, and therefore the photographs in Figure 7 show only one side of the microhole. From the photographs it can be observed that the fatigue cracks in hydrogen-charged material tend to grow more linearly than in uncharged material. Whereas in the hydrogen-charged material the slip bands occur over a broad region, it is clear that in the uncharged material the slip bands are localized near the fatigue cracks.

[0050] Figure 8 is a graph showing the results of fatigue testing of SUS316L. This figure shows the fatigue test results of materials with a hydrogen content of 0.4 mass ppm and 2.6 mass ppm when uncharged, and after the material with a hydrogen content of 2.6 mass ppm was charged with hydrogen to raise the content to 3.9 mass ppm. The repetition rate until the fatigue crack reached a length of 200 μm was 1.5 Hz. When the length of the fatigue crack became 200 μm, the repetition rate was changed from 1.5 Hz to 0.0015 Hz. The fatigue cracks grew in material with a hydrogen content of 2.6 mass ppm and 3.9 mass ppm.

[0051] However, fatigue cracks grew only slightly in the material with a hydrogen content of 0.4 mass ppm. Figure 9 is a graph showing the result of the fatigue testing of SUS316L. This figure shows the fatigue test results of materials with a hydrogen content of 0.4 mass ppm and 2.6 mass ppm when uncharged, and results after the material with a hydrogen content of 2.6 mass ppm was charged with hydrogen to raise the content to 3.9 mass ppm and 5.1 mass ppm. The repetition rates were 1.5 Hz and 0.0015 Hz.

[0052] From this graph it is clear that the fatigue cracks have grown in the material with a hydrogen content of 2.6 mass ppm and in the same material charged with hydrogen to a content of 3.9 mass ppm and 5.1 mass ppm. It is clear that when the repetition rate was a low 0.0015 Hz, the fatigue crack growth rate is faster than at a repetition rate of 1.5 Hz. However, it is also clear that in material with a hydrogen content of 0.4 mass ppm the fatigue crack growth rate is slower at repetition rates of both 0.0015 Hz and 1.5 Hz. This illustrates the fact that fatigue cracks do not grow much when the hydrogen content in the material is 0.4 mass ppm or less.

[0053] Figure 10 is a conceptual drawing showing the situation wherein the diffusible hydrogen and the non-diffusible hydrogen diffuse through the transformed martensitic phase. In the figure the tip of the fatigue crack undergoes martensitic transformation, and the diffusible hydrogen and non-diffusible hydrogen diffuse via the martensitic phase. In other words, the hydrogen moves using the martensitic phase with its fast diffusion rate as a passageway, and it accumulates at the tip of the fatigue crack. This is a phenomenon related to hydrogen diffusion and migration time. The rate of diffusion of the hydrogen in the austenitic phase (FCC) is four decimal places 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

[0054] Therefore, through the above test it was shown 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, and the martensitic transformation of the fatigue crack tip (transformation from FCC to BCC) affects this.

Relationship between fatigue test rate and fatigue crack growth rate

[0055] In addition, from Figure 9 showing the above test results, it is clear that the fatigue crack growth rate accelerates in austenitic stainless steel such as SUS316L if the fatigue test rate is slow. In a similar manner, as shown in Figure 6, the fatigue crack growth rate is faster in hydrogen-charged material such as the test pieces charged with diffusible hydrogen than in uncharged material. As shown in Figures 8 and 9, fatigue cracks grow very little in material with a hydrogen content of 0.4 mass ppm or less. Thus, the effect of slowing the fatigue test rate is a phenomenon related to hydrogen diffusion and migration time (the diffusion rate is four decimal places slower in FCC than in BCC).

[0056] Below the alloying components in the austenitic stainless steel of the present invention, the content thereof, and the manufacturing steps, etc., stipulated in the manufacturing process of the present invention are explained.

Austenitic stainless steel

[0057] Austenitic stainless steel is also called Cr-Ni stainless steel, and it involves the addition of chromium and nickel to iron. The principal components of austenitic stainless steel are iron, chromium, and nickel with various additives shown in Table 2 below.

[0058] Table 2 below shows preferred examples of the austenitic stainless steel of the present invention, but the mode of the present invention is by no means limited thereto.

[0059]

[Table 2]

Component	Composition 1 (mass ratio)	Composition 2 (mass ratio)
C	≤0.030	≤0.08
Si	≤1.00	≤1.50
Mn	≤2.00	≤2.00
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	≤3.00
Al	-	≤0.35
N	-	≤0.50
Ti	-	≤2.35
V	-	≤0.50
B	-	≤0.010
H	≤0.00007 (0.7ppm)	≤0.00007 (0.7ppm)
Other	Remainder Fe and inevitable impurities	Remainder Fe and inevitable impurities

Chemical composition of austenitic stainless steel

[0060] Chromium is added to iron to improve corrosion resistance. Nickel is added to iron in combination with chromium to increase corrosion resistance. Nickel and manganese are elements for insuring nonmagnetic properties after cold rolling. The nickel content must be 10.0 mass% or more to insure the nonmagnetic properties after cold rolling. In addition, it is necessary to adjust the content of nickel according to the content of silicon and manganese so that a stress-induced martensitic phase of ≥1 vol% does not occur. Manganese also has the effect of improving the solid solubility of nitrogen.

[0061] Carbon is an element for a strong austenite formation. In addition, carbon is an effective element for enhancing the strength of stainless steel. When an excess of carbon is added, coarse chromium carbides precipitate during the recrystallization process, and that causes a decrease in intergranular corrosion resistance and fatigue properties. Silicon is added for deacidification and strengthening of the solid solution. Because generation of the martensitic phase during cold-working is promoted when the content of silicon increases, adding only a small amount thereof is preferred. Nitrogen brings about solution hardening.

[0062] Molybdenum is added for improved corrosion resistance. In addition, it has the effect of bringing about the fine dispersion of carbonitrides in the aging treatment. Titanium is an effective element for precipitation hardening and is added to increase the strength brought about by the aging treatment. Boron is an effective alloying component for the prevention of edge cracks in the hot rolled steel area caused by the difference in the deformation resistance between the δ-ferrite phase in the hot working temperature region and the austenitic phase. Aluminum is an element added for deacidification during steelmaking and is effective in precipitation hardening in a similar manner to titanium.

[0063] The mode for carrying out the present invention can also be used by adding elements such as niobium, copper, etc., as needed in addition to the elements described in Table 2 above. Niobium can serve as a substitute for titanium.

Austenitic phase

[0064] Austenitic stainless steel wherein the austenitic phase is essentially 100% of the total volume is preferred. Austenitic stainless steel having no martensitic phase contained therein is preferable.

Other properties

[0065] The average crystalline particle diameter is preferably about 50 μm or less. In modern materials the average crystalline particle diameter is about 50 μm, but a smaller the average crystalline particle diameter is preferred.

Hydrogen removal treatment by heating

[0066] The hydrogen removal treatment involving the heating of austenitic stainless steel will now be described. The inventors of the present invention ascertained that non-diffusible hydrogen takes part in fatigue crack growth, and based upon that discovery, the heat treatment described below is performed to remove the non-diffusible hydrogen and the diffusible hydrogen present in austenitic stainless steel.

[0067] Removal of the diffusible hydrogen and the non-diffusible hydrogen involves performing a heat treatment on the austenitic stainless steel at a heating temperature of 200°C or more. The heat treatment is performed in a vacuum. The vacuum environment is 0.2 Pa or less. Moreover, for the heat treatment the austenitic stainless steel is maintained under vacuum at the heating temperature for 460 hours or less. The temperature of the heat treatment is lower than the sensitization temperature, which is the temperature at which the carbides of chromium (Cr) in the austenitic stainless steel precipitate due to heating.

[0068] For the austenitic stainless steels shown in Table 1 and Table 2, for example, the upper limit of the heating temperature is 500°C. As a result, both the non-diffusible hydrogen, and the diffusible hydrogen (which are present in austenitic stainless steel, diffuse via the stress-induced martensitic phase brought about by cyclic loading, concentrate in the cracks undergoing concentrated stress, and cause hydrogen embrittlement) can be removed.

[0069] By such a heat treatment it is possible to remove from austenitic stainless steel the diffusible hydrogen and the non-diffusible hydrogen that cause hydrogen embrittlement therein, and thereby adjust the hydrogen (H) contained in austenitic stainless steel to 0.00007 mass% (0.7 mass ppm) or less. The preferred content of hydrogen (H) in austenitic stainless steel after this heat treatment is ≤0.00004 mass% (≤0.4 mass ppm), and ≤0.00001 mass% (≤0.1 mass ppm) is even more preferred.

[0070] Thus, it is possible to provide an excellent austenitic stainless steel wherein the content of hydrogen therein is less than in the prior art austenitic stainless steels, and acceleration of fatigue crack growth does not occur even with cyclic loading involving a long cycle time.

Additional Experimental Example 1

[0071] The experiment was performed on a heat-treated test piece of SUS316. The test piece was a rod 7 mm in diameter. For the TDS measurement a disk 7 mm in diameter and 0.8 mm in thickness was cut from the rod. For the experiment the test piece was heat-treated at 800°C for 20 minutes. The atmospheres during the experiment were an air atmosphere, a vacuum atmosphere (approximately 0.006 Pa), and an argon gas atmosphere. The heat treatment was performed while supplying argon gas thereto. The heating rate for the TDS measurement was 0.5°C/second up to 700°C. The escaped hydrogen was measured for heating up to 700°C.

[0072] The measurement was performed with a thermal desorption spectrometer model EMD-WA1000S/H manufactured by ESCO, Ltd. (Musashino, Tokyo). Figure 12 shows the measurement results. In the graph the horizontal axis shows the measurement temperature, and the vertical axis shows the hydrogen intensity. The hydrogen concentration of the test piece that had not been heat-treated was 1.5 mass ppm. When the heat treatment was performed in air, the hydrogen concentration of the test piece became 0.7 mass ppm. When the heat treatment was performed in a vacuum, the hydrogen concentration of the test piece became 0.4 mass ppm. When the heat treatment was performed under with the argon gas flow, the hydrogen concentration decreased to 0.4 mass ppm.

Additional Experimental Example 2

[0073] The experiment was performed on a heat-treated test piece of SUH660. The test piece was a rod 7 mm in diameter. For the TDS measurement a disk 7 mm in diameter and 0.8 mm in thickness was cut from the rod. For the experiment the test piece was heat-treated at 720°C for 16 hours. The atmosphere during the experiment was a vacuum atmosphere (approximately 0.006 Pa). The hydrogen concentration was 1.3 ppm before the aging treatment and 0.6 ppm after the aging treatment.

[0074] In this manner, an aging treatment and the like was performed during the manufacturing process of stainless steel, and the hydrogen contained therein could be removed. The heating rate for the TDS measurement was 0.33°C/second up to 600°C. The escaped hydrogen was measured for heating up to 600°C. The measurement was performed with a thermal desorption spectrometer model EMD-WA1000S/H manufactured by ESCO, Ltd. (Musashino, Tokyo). Figure 13 shows the measurement results. The horizontal axis in the graph shows the measurement temperature, and vertical axis shows the hydrogen escape strength.

INDUSTRIAL APPLICABILITY

[0075] The present invention is good for use in fields where corrosion resistance and high pressure hydrogen are necessary. More specifically, the present invention is good for use in metal gaskets, various types of valves used in automobiles, springs, steel belts, cutting blade material, fuel cells, and material for valves, springs, etc., surrounding fuel cell systems.

Claims

1. An austenitic stainless steel having an austenitic phase in which a crystalline structure is a face centered cubic lattice structure,
wherein diffusible hydrogen and non-diffusible hydrogen, which are cause of hydrogen embrittlement in the austenitic stainless steel, are removed therefrom such that the hydrogen (H) contained in the austenitic stainless steel is removed to a level of 0.00007 mass% (0.7 mass ppm) or less.

2. The austenitic stainless steel according to claim 1,
wherein the diffusible hydrogen and non-diffusible hydrogen are removed therefrom such that the hydrogen (H) is removed to a level of 0.00004 mass% (0.4 mass ppm) or less.

3. The austenitic stainless steel according to claim 2,
wherein the diffusible hydrogen and non-diffusible hydrogen are removed therefrom such that the hydrogen (H) is removed to a level of 0.00001 mass% (0.1 mass ppm) or less.

4. The austenitic stainless steel according to any one of claims 1 to 3,
wherein the austenitic stainless steel is heat-treated at a heating temperature of 200°C or higher to remove the diffusible and non-diffusible hydrogen therefrom.

5. The austenitic stainless steel according to claim 4,
wherein the heating temperature is a temperature from 200°C to 500°C.

6. A process for removing hydrogen from an austenitic stainless steel, in which the austenitic stainless steel having an austenitic phase in which a crystalline structure is a face centered cubic lattice structure is heat-treated in a heat treatment to remove the hydrogen present in the austenitic stainless steel,
wherein the austenitic stainless steel is heated to a heating temperature of 200°C or higher to remove the diffusible hydrogen and non-diffusible hydrogen in the austenitic stainless steel to a level of 0.00007 mass% (0.7 mass ppm) or less.

7. The process for removing hydrogen from austenitic stainless steel according to claim 6,
wherein the heating temperature is a temperature from 200°C to 500°C, and both the diffusible hydrogen and non-diffusible hydrogen, which are present in the austenitic stainless steel, diffuse via the stress-induced martensitic phase brought about by cyclic loading, concentrate in the cracks undergoing concentrated stress, and cause hydrogen embrittlement therein, are removed therefrom such that the hydrogen (H) contained therein is removed to a level of 0.00007 mass% (0.7 mass ppm) or less.

8. The process for removing hydrogen from austenitic stainless steel according to claim 6,
wherein the austenitic stainless steel is maintained at a temperature from 200°C to 500°C, which is a temperature lower than the sensitization temperature at which chromium (Cr) carbide in the austenitic stainless steel precipitates due to the heat, for 460 hours or less, and
both the diffusible hydrogen and non-diffusible hydrogen, which cause hydrogen embrittlement in the austenitic stainless steel, are removed therefrom such that the hydrogen (H) contained in the austenitic stainless steel is removed to a level of 0.00004 mass% (0.4 mass ppm) or less.

9. The process for removing hydrogen from an austenitic stainless steel according to claim 7 or 8,
wherein the hydrogen (H) contained in the austenitic stainless steel is removed to a level of 0.00001 mass% (0.1 mass ppm) or less.

10. The process for removing hydrogen from an austenitic stainless steel according to claim 6,
wherein the austenitic stainless steel is maintained at the heating temperature and in a temperature range below a melting point thereof for 30 seconds or more during the manufacturing process thereof to remove the diffusible hydrogen and non-diffusible hydrogen contained therein to a level of 0.00007 mass% (0.7 mass ppm) or less.

11. The process for removing hydrogen from austenitic stainless steel according to claim 10,
wherein the heating temperature in the heat treatment to remove the hydrogen present therein is 700°C or more and also in a temperature range below the melting point of the austenitic stainless steel.

12. The process for removing hydrogen from austenitic stainless steel according to claim 11,
wherein the heating temperature in the heat treatment to remove the hydrogen present therein is 920°C or higher, and the diffusible hydrogen and non-diffusible hydrogen therein are removed to a level of 0.00004 mass% (0.4 mass ppm) or less.

Fig.1

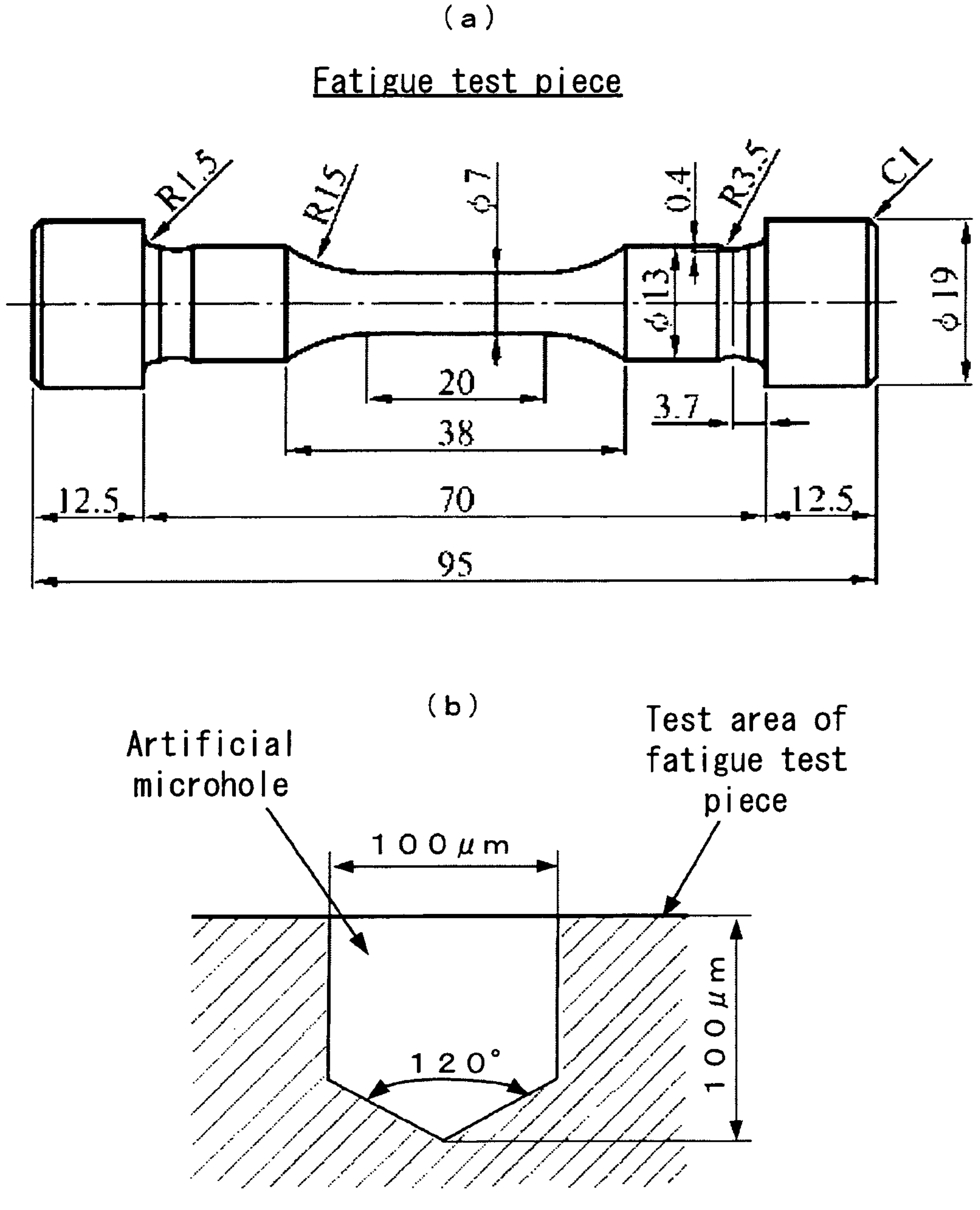

(a)
Fatigue test piece
R1.5
R15
φ7
0.4
R3.5
C1
φ13
φ19
20
38
3.7
12.5
70
12.5
95
(b)
Artificial microhole
Test area of fatigue test piece
100μm
120°
100μm

Fig.2

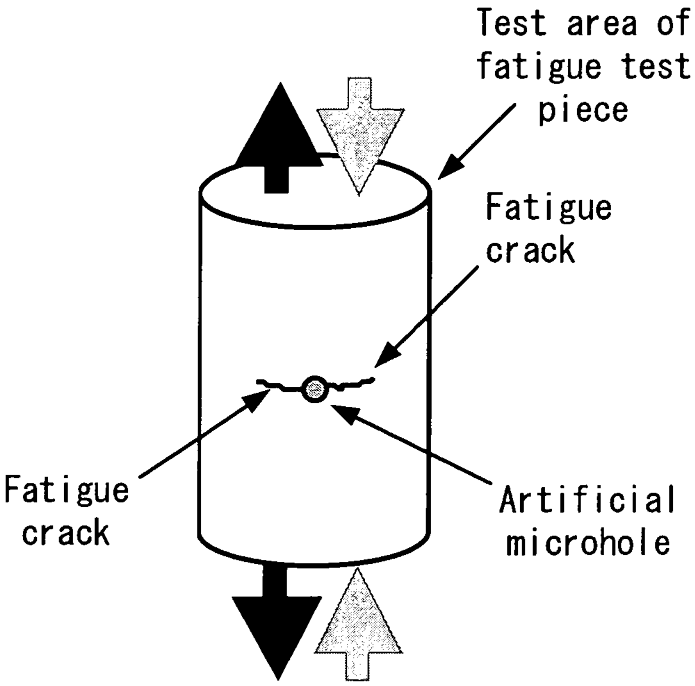

Test area of fatigue test piece
Fatigue crack
Fatigue crack
Artificial microhole

Fig.3

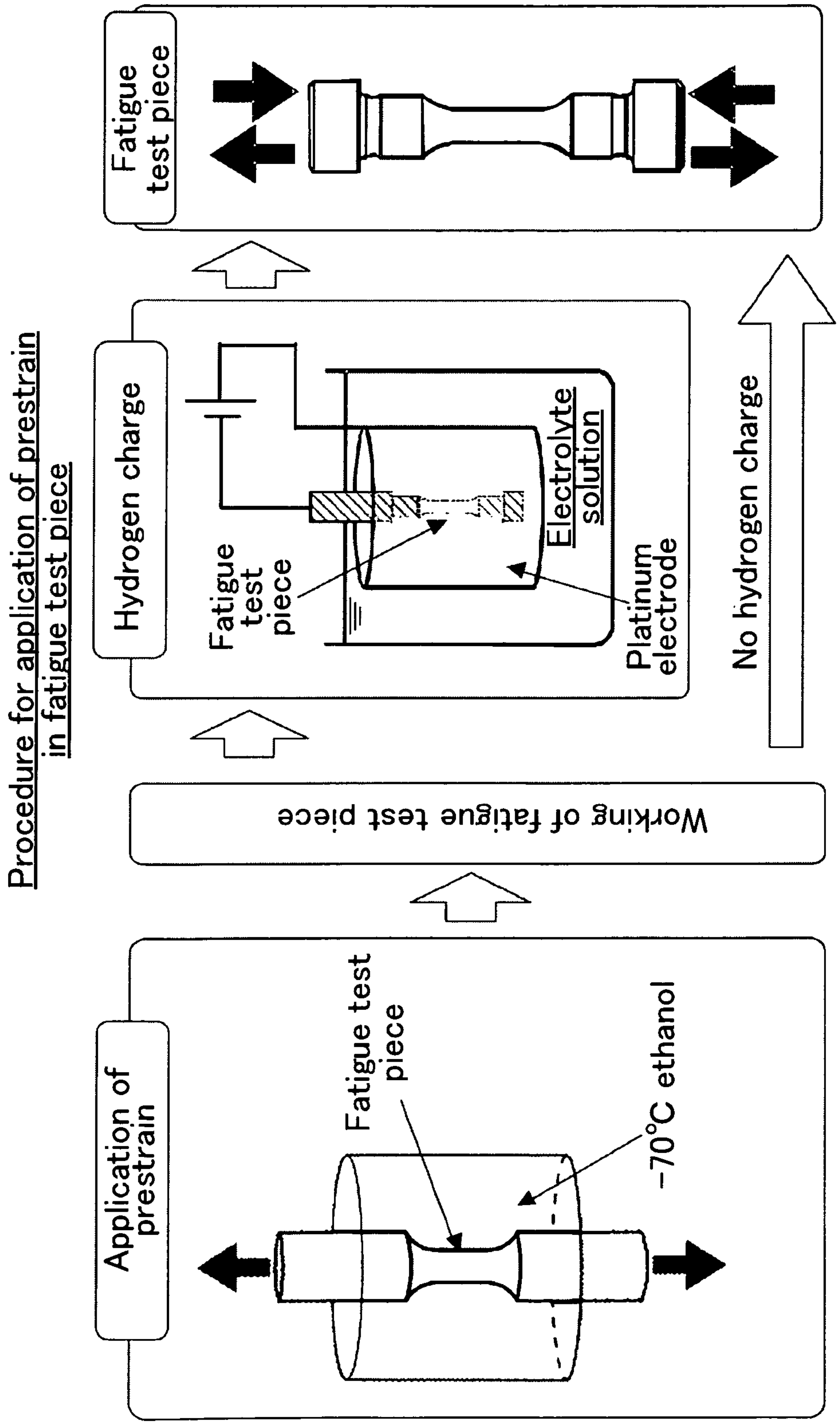

Procedure for application of prestrain in fatigue test piece
Application of prestrain
Fatigue test piece
-70°C ethanol
Working of fatigue test piece
Hydrogen charge
Fatigue test piece
Electrolyte solution
Platinum electrode
No hydrogen charge
Fatigue test piece

Fig.4

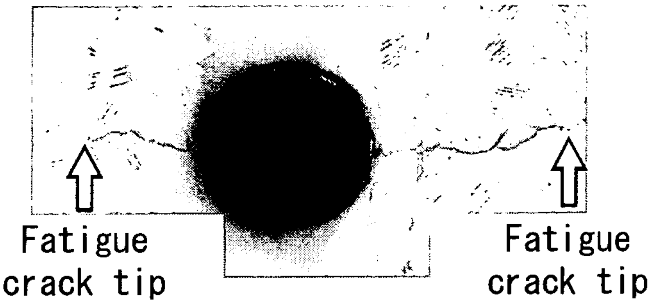
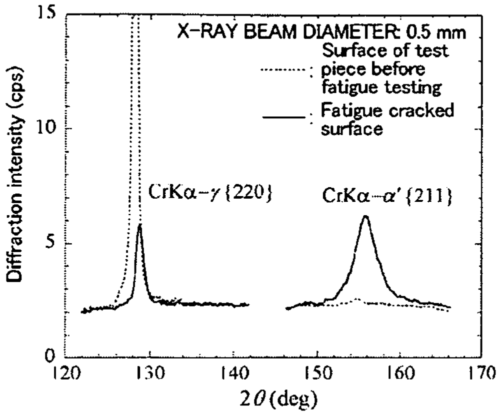


Fig.5

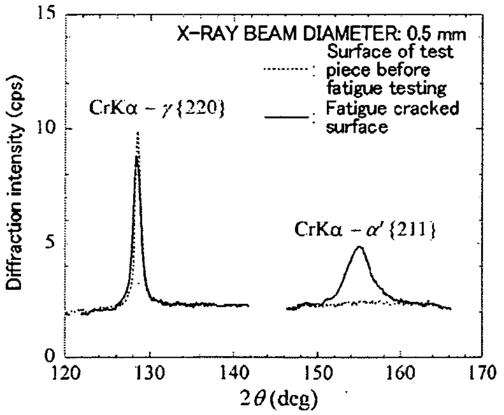
(a)

SUS304 (σ = 240 MPa, b = 0.35 mm)



(b)

SUS316 (σ= 240 MPa, b = 0.35 mm)



(c)

SUS316L (σ = 260 MPa, b = 0.35 mm)

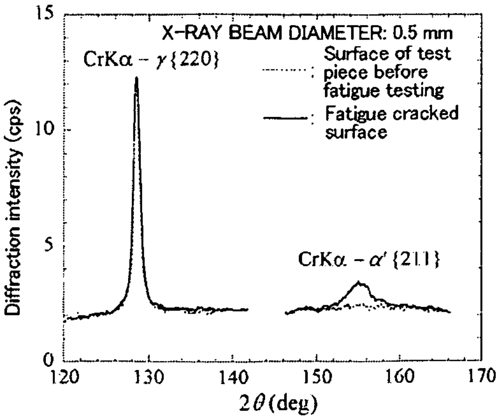
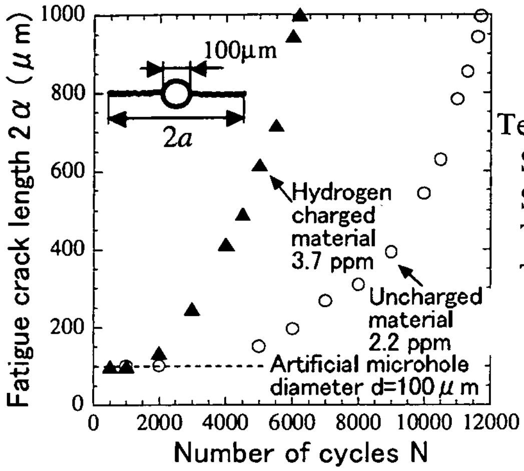


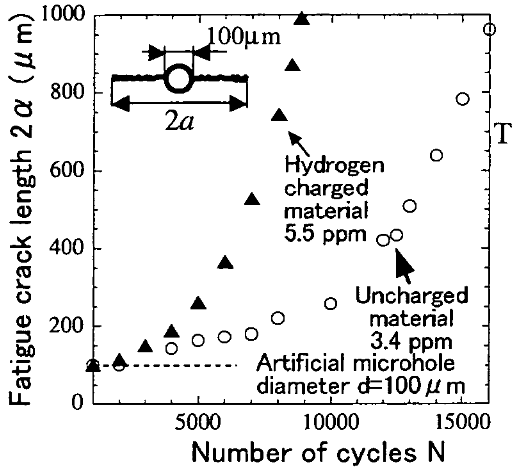
Fig.6

(a)



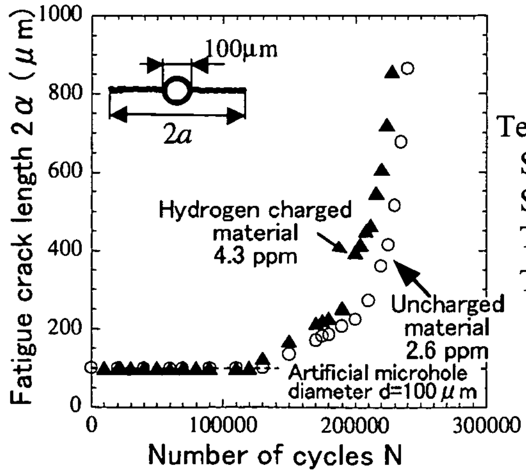
Test conditions:
SUS304 (HV = 176)
Stress amplitude: 280 MPa
Test frequency: 1.2 Hz
Test temperature: 14 to 25°C

(b)



Test conditions:
SUS316 (HV = 161)
Stress amplitude: 260 MPa
Test frequency: 1.2 Hz
Test temperature: 11 to 25°C

(c)



Test conditions:
SUS316L (HV = 157)
Stress amplitude: 260 MPa
Test frequency: 5 Hz
Test temperature: 18 to 34°C

Fig.7

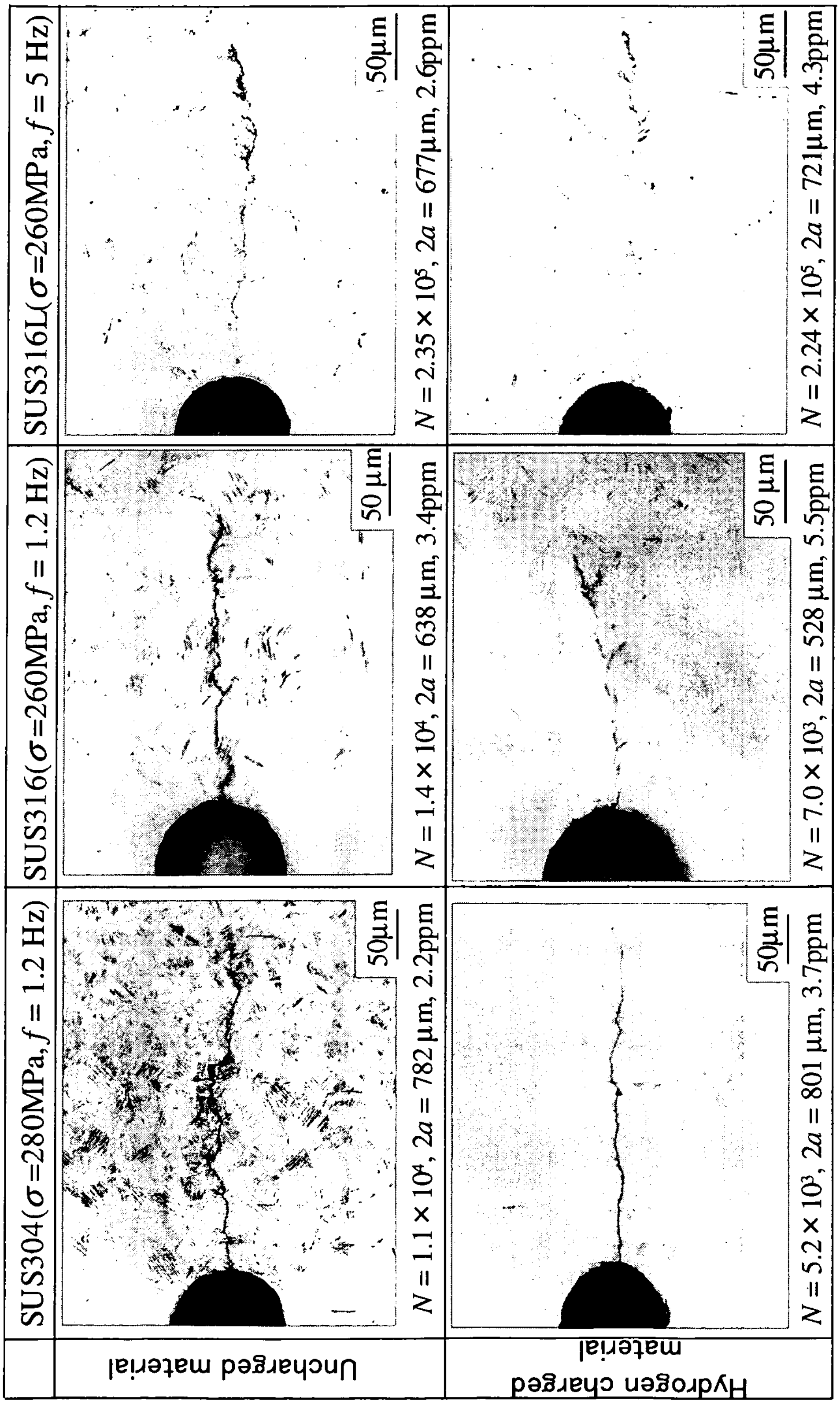

SUS304(σ=280MPa, f = 1.2 Hz)
SUS316(σ=260MPa, f = 1.2 Hz)
SUS316L(σ=260MPa, f = 5 Hz)
Uncharged material
Hydrogen charged material
50µm
50 µm
N = 1.1 × 10⁴, 2a = 782 µm, 2.2ppm
N = 1.4 × 10⁴, 2a = 638 µm, 3.4ppm
N = 2.35 × 10⁵, 2a = 677µm, 2.6ppm
N = 5.2 × 10³, 2a = 801 µm, 3.7ppm
N = 7.0 × 10³, 2a = 528 µm, 5.5ppm
N = 2.24 × 10⁵, 2a = 721µm, 4.3ppm

Fig.8

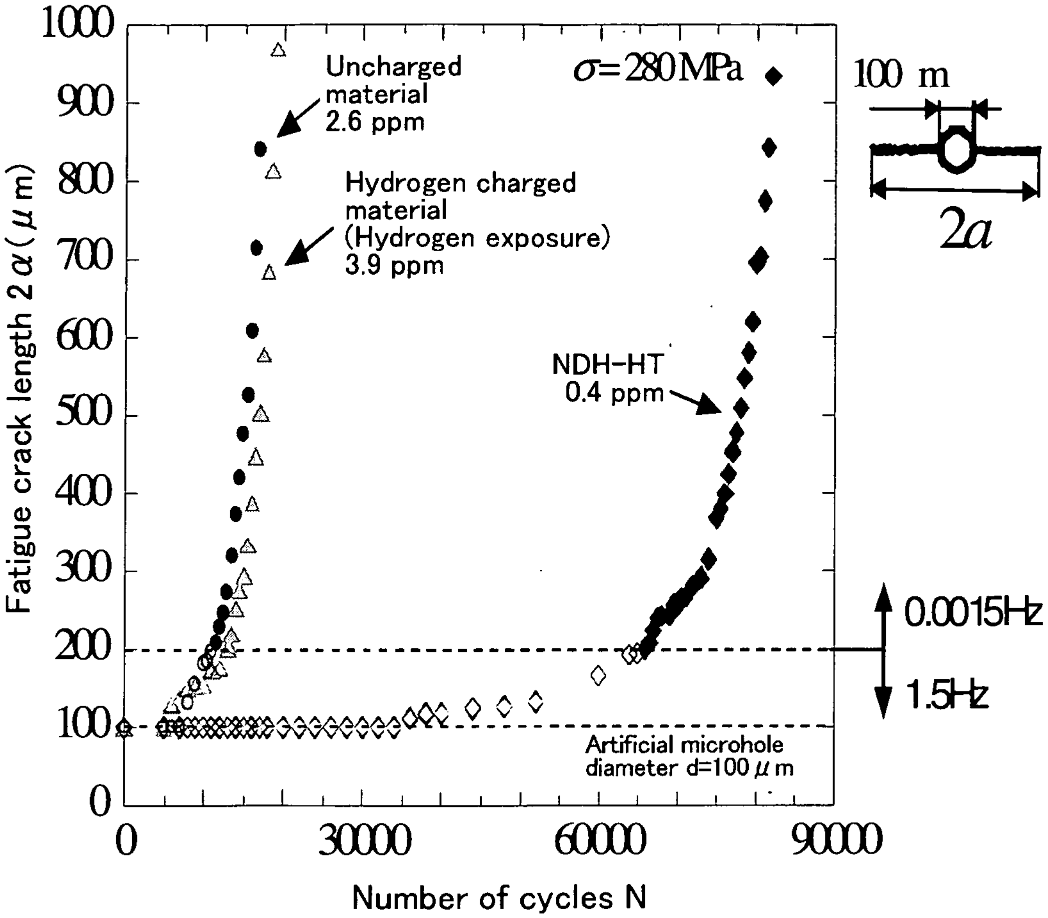

1000
900
800
700
600
500
400
300
200
100
0
Fatigue crack length 2α(μm)
0
30000
60000
90000
Number of cycles N
σ=280MPa
Uncharged material 2.6 ppm
Hydrogen charged material (Hydrogen exposure) 3.9 ppm
NDH-HT 0.4 ppm
Artificial microhole diameter d=100μm
100 m
2a
0.0015Hz
1.5Hz

Fig.9

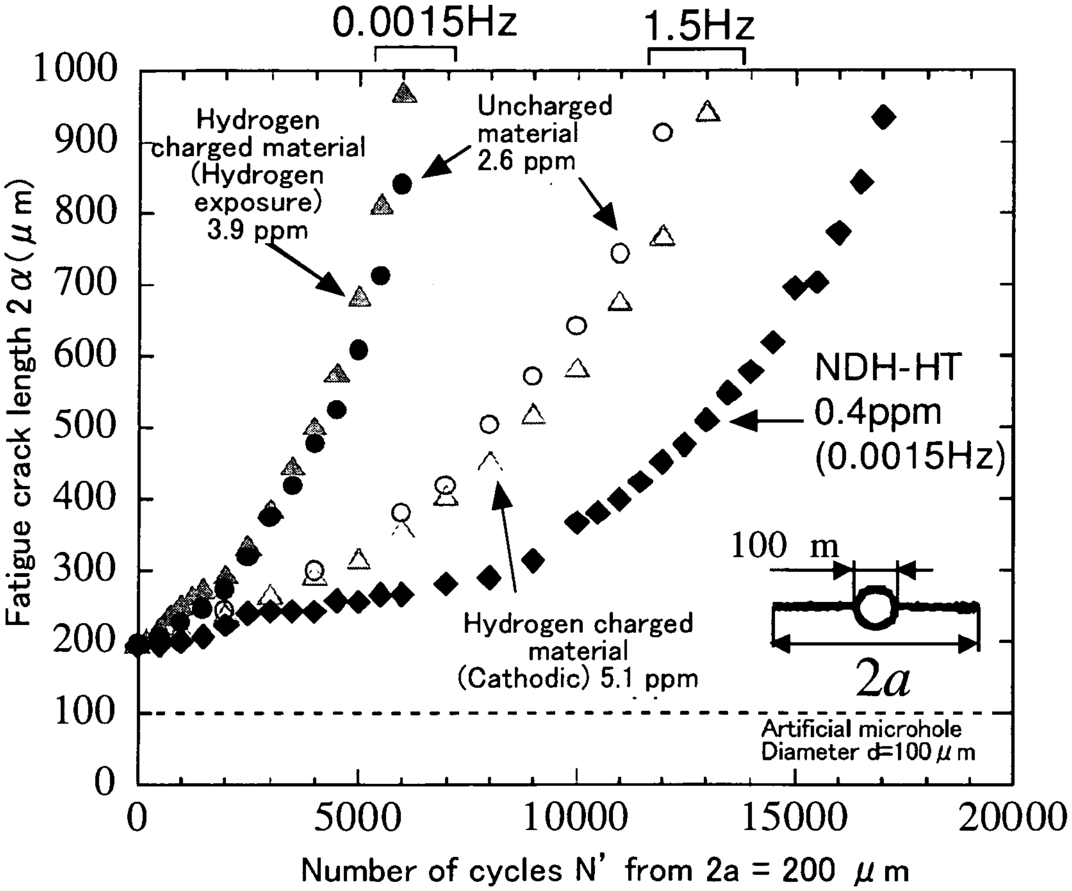

0.0015Hz
1.5Hz
Hydrogen charged material (Hydrogen exposure) 3.9 ppm
Uncharged material 2.6 ppm
NDH-HT 0.4ppm (0.0015Hz)
Hydrogen charged material (Cathodic) 5.1 ppm
100 m
2a
Artificial microhole Diameter d=100 μm
Fatigue crack length 2a (μm)
Number of cycles N' from 2a = 200 μm
0
100
200
300
400
500
600
700
800
900
1000
0
5000
10000
15000
20000

Fig.10

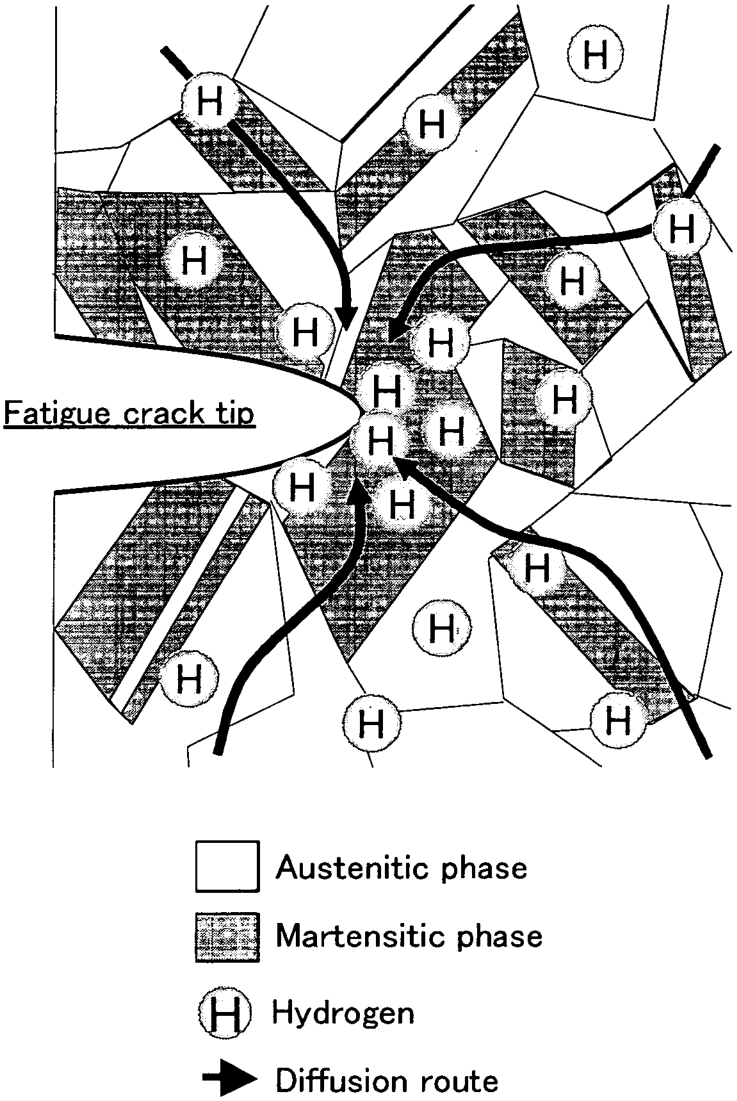
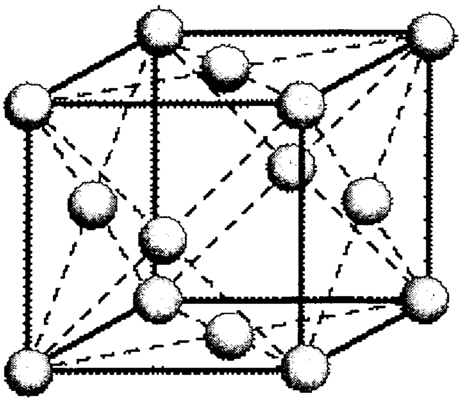

H
Fatigue crack tip
Austenitic phase
Martensitic phase
Hydrogen
Diffusion route

Fig.11

(a)

Face centered cubic lattice (FCC)



(b)

Body centered cubic lattice (BCC)

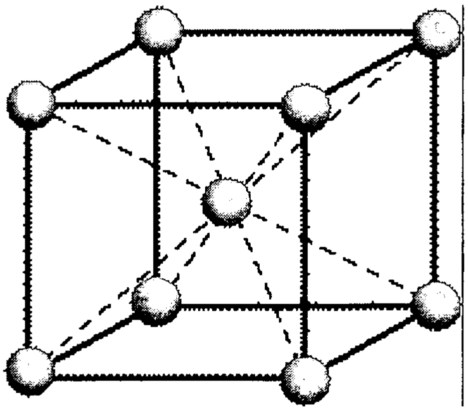


Fig.12

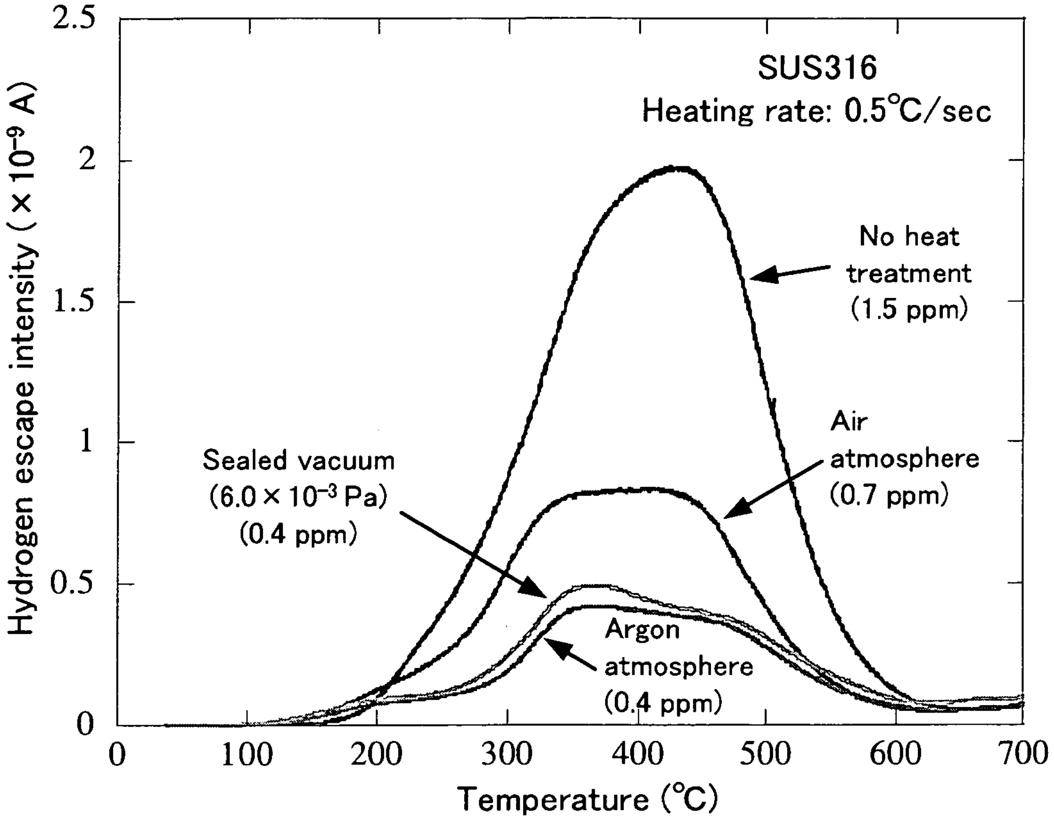
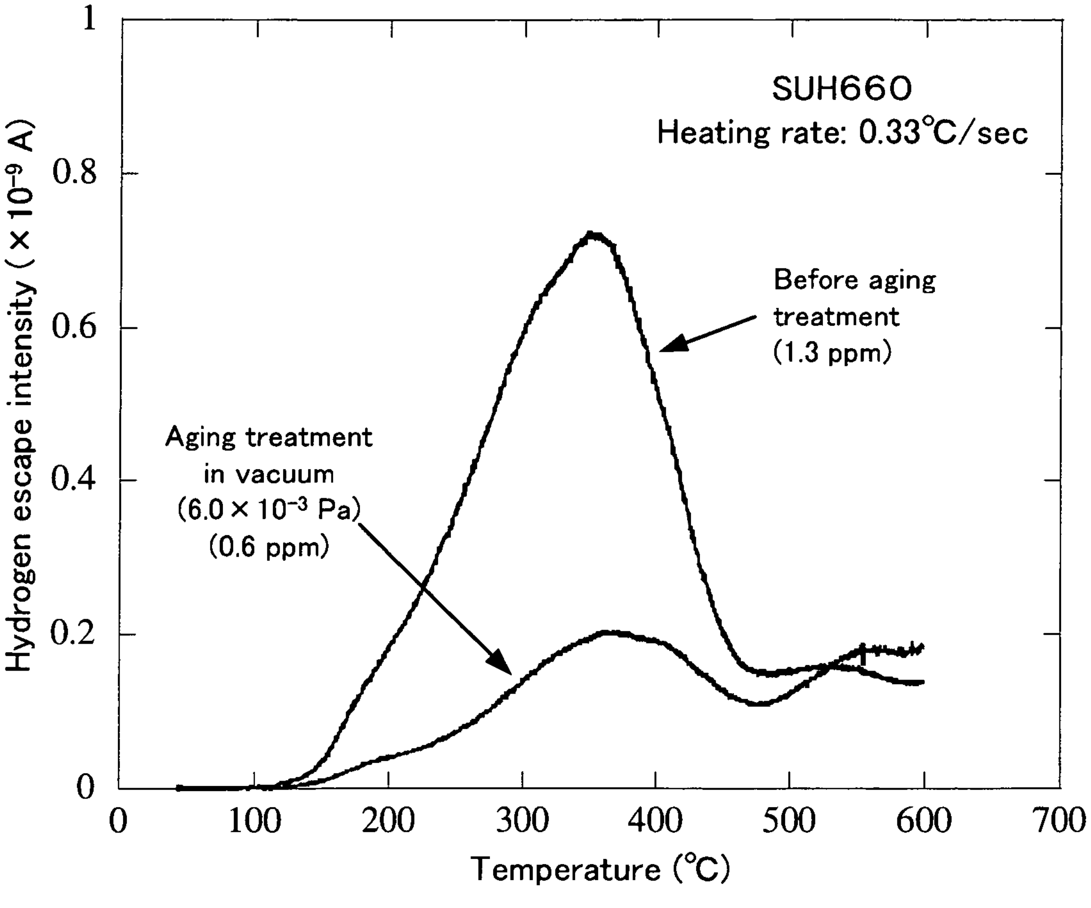

2.5
2
1.5
1
0.5
0
Hydrogen escape intensity (×10⁻⁹ A)
0
100
200
300
400
500
600
700
Temperature (℃)
SUS316
Heating rate: 0.5℃/sec
No heat treatment (1.5 ppm)
Air atmosphere (0.7 ppm)
Sealed vacuum (6.0×10⁻³ Pa) (0.4 ppm)
Argon atmosphere (0.4 ppm)

Fig.13


SUH660
Heating rate: 0.33°C/sec
Before aging treatment (1.3 ppm)
Aging treatment in vacuum (6.0×10^{-3} Pa) (0.6 ppm)
Hydrogen escape intensity ($\times 10^{-9}$ A)
0
0.2
0.4
0.6
0.8
1
0
100
200
300
400
500
600
700
Temperature (°C)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2007/069589

A. CLASSIFICATION OF SUBJECT MATTER
C22C38/00(2006.01)i, *C21D3/06*(2006.01)i, *C21D6/00*(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)
C22C38/00-38/60, C21D3/06, C21D6/00

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	1996-2007
Kokai Jitsuyo Shinan Koho	1971-2007	Toroku Jitsuyo Shinan Koho	1994-2007

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
JSTPlus(JDream2)

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 2005-298932 A (Nippon Steel & Sumikin Stainless Steel Corp.), 27 October, 2005 (27.10.05), Table 4 (Family: none)	1 2-12
X Y	JP 10-121208 A (Nippon Steel Corp.), 12 May, 1998 (12.05.98), Par. No. [0015]; table 2 (Family: none)	1 2-12
Y	WO 2004/22809 A1 (National Institute of Advanced Industrial Science and Technology), 18 March, 2004 (18.03.04), Page 4, line 31 & EP 1548139 A1 & US 2006/104850 A1	2-12

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

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"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)
"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 26 December, 2007 (26.12.07)	Date of mailing of the international search report 15 January, 2008 (15.01.08)
Name and mailing address of the ISA/ Japanese Patent Office Facsimile No.	Authorized officer Telephone No.

Form PCT/ISA/210 (second sheet) (April 2007)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2007/069589

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP 11-181517 A (Nippon Steel Corp.), 06 July, 1999 (06.07.99), Par. Nos. [0011], [0012] (Family: none)	2-12
A	JP 6-49538 A (Nippon Nuclear Fuel Development Co., Ltd.), 22 February, 1994 (22.02.94), Par. No. [0018] (Family: none)	1-12

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