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(54) DUPLEX STAINLESS STEEL, AND DUPLEX STAINLESS STEEL STRUCTURE, MARINE STRUCTURE, PETROLEUM/GAS ENVIRONMENT STRUCTURE, PUMP IMPELLER, PUMP CASING, AND FLOW ADJUSTMENT VALVE BODY USING SAME

ROSTFREIER DUPLEXSTAHL UND STRUKTUR AUS DEM ROSTFREIEN DUPLEXSTAHL, MEERESSTRUKTUR, ERDÖL/GAS-UMGEBUNGSSTRUKTUR, PUMPENLAUFRAD, PUMPENGEHÄUSE UND VENTILKÖRPER ZUR DURCHFLUSSEINSTELLUNG DAMIT

ACIER INOXYDABLE DUPLEX ET STRUCTURE EN ACIER INOXYDABLE DUPLEX, STRUCTURE MARINE, STRUCTURE POUR ENVIRONNEMENT PÉTROLIER/GAZIER, ROTOR DE POMPE, CORPS DE POMPE ET CORPS DE SOUPAPE DE RÉGLAGE DE DÉBIT UTILISANT CET ACIER

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(56) References cited:

EP-A1- 1 803 832	**EP-A2- 0 818 552**
WO-A1-2012/111536	**JP-A- S5 441 214**
JP-A- 2004 520 491	**JP-A- 2005 520 934**
US-A- 4 055 448	

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Description

Technical Field

[0001] The present invention relates to duplex stainless steels and structures using the same.

Background Art

[0002] Duplex stainless steels mainly have a two-phase metal structure including a ferrite phase (alpha phase) and an austenite phase (gamma phase). The duplex stainless steels have a high strength and excel in pitting corrosion resistance and crevice corrosion resistance in a chloride/sulfide environment. Using the properties, the duplex stainless steels are widely used as materials for marine structures and for petrochemical industries. The duplex stainless steels, however, are known to have inferior toughness when exposed to a high temperature under some manufacturing conditions or working conditions. This is because of the formation of hard and fragile intermetallic compounds (sigma phase, chi phase, and Laves phase) mainly containing Cr, Mo, or another element as a principal component; and an embrittlement phase of nitrides/carbides.

[0003] The duplex stainless steels have better corrosion resistance with an increasing pitting resistance equivalent number (PREW) specified by an expression given as follows:

$$(\mathrm{PREW}) = \%\mathrm{Cr} + 3.3 \times (\%\mathrm{Mo} + 0.5 \times \%\mathrm{W}) + 30 \times \%\mathrm{N}$$

where %Cr, %Mo, %W, and %N are contents (in mass percent) of Cr, Mo, W, and N, respectively.

[0004] The duplex stainless steels, however, suffer from the precipitation of the intermetallic compounds with increasing contents of Cr, Mo, and W. The duplex stainless steels often suffer from defects caused by blowhole formation during manufacturing because nitrides are precipitated in larger amounts with an increasing nitrogen content, if the duplex stainless steels have an excessively high nitrogen content.

[0005] In manufacturing processes of a duplex stainless steel, a work is subjected to a solution heat treatment at 950°C to 1200°C to give an appropriate phase ratio between the ferrite phase and austenite phase. The work is then subjected to rapid cooling from the solution heat treatment temperature down to room temperature typically by water cooling. This process is performed to avoid the precipitation of the embrittlement phase and to avoid 475°C embrittlement. The process, however, disadvantageously impedes stable manufacturing of large-sized structures, particularly of thick-walled structures prepared by casting or forging. This is because the embrittlement phase is precipitated inside the material steel due to the difference in cooling rate between the surface and the inside of the steel. The disadvantage is, however, trivial in thin-walled materials such as thin sheets and pipes.

[0006] The duplex stainless steel also disadvantageously suffers from reduction in toughness due to the embrittlement phase precipitation in a weld heat affected zone or as a result of annealing performed so as typically to reduce the residual stress.

[0007] There have been proposed techniques for suppressing the embrittlement phase upon manufacturing or use while focusing on steel chemical compositions.

[0008] Patent Literature 1 (PTL 1) discloses a super duplex stainless steel in order to suppress the formation of sigma phase, chi phase, and other intermetallic compounds that adversely affect corrosion resistance and mechanical properties. The super duplex stainless steel contains, in weight percent, Cr in a content of 21.0% to 38.0%, Ni in a content of 3.0% to 12.0%, Mo in a content of 1.5% to 6.5%, W in a content of 0% to 6.5%, Si in a content of 3.0% or less, Al in a content of 1.0% or less, Mn in a content of 8.0% or less, N in a content of 0.2% to 0.7%, C in a content of 0.1% or less; and at least one element selected from the group consisting of B in a content of 0.1% or less, Cu in a content of 3.0% or less, and Co in a content of 3.0% or less. The super duplex stainless steel desirably further contains at least one element selected from the group consisting of Ca in a content of 0.5% or less, Mg in a content of 0.5% or less, Ta in a content of 0.5% or less, Nb in a content of 0.5% or less, Ti in a content of 1.5% or less, Zr in a content of 1.0% or less, Sn in a content of 1.0% or less, and In in a content of 1.0% or less, as described in the literature.
Steel compositions containing Nb are disclosed in EP 0 818 552 A2 and US 4 055 448 A.

Citation List

Patent Literature

[0009] PTL 1: Japanese Patent Application Laid-Open No. 2011-174183 corresponding to EP 1 803 832 A1

Summary of Invention

Technical Problem

[0010] The super duplex stainless steel in PTL 1 may suffer from embrittlement progression, because the steel has a high nitrogen content and thereby often suffers from nitride formation; and this may impede appropriate dissolution of added elements in the alloy.

[0011] An object of the present invention is to suppress the formation of intermetallic compounds (sigma phase, chi phase, and Laves phase) and nitrides in a duplex stainless steel and to help the duplex stainless steel to have better corrosion resistance, embrittlement resistance, productivity, weldability, and thermal processability.

Solution to Problem

[0012] The invention provides a duplex stainless steel, a structure using the steel and a method for manufacturing the steel in accordance with the attached claims.

Advantageous Effects of Invention

[0013] The present invention, in the aspect, adapts a tantalum-containing duplex stainless steel to contain nitrogen in a low content and helps the duplex stainless steel to less suffer from nitride formation. The aspect also helps the duplex stainless steel to have better corrosion resistance, embrittlement resistance, productivity, weldability, and thermal processability because metallic tantalum not forming nitrides inhibits the diffusion or migration of elements that form intermetallic compounds.

Brief Description of Drawings

[0014]

Figure 1A is a conceptual diagram illustrating an embrittlement phase formation mechanism in a customary duplex stainless steel.
Figure 1B is a conceptual diagram illustrating an embrittlement phase formation suppressing mechanism in a duplex stainless steel according to an embodiment of the present invention.
Figure 2A is an external view image of a Sample Steel A prepared by forging.
Figure 2B is an external view image of a Sample Steel B prepared by forging.
Figure 2C is an external view image of a Sample Steel C prepared by forging.
Figure 3A depicts a metal structure observation result of Sample Steel A.
Figure 3B depicts a metal structure observation result of Sample Steel B.
Figure 3C depicts a metal structure observation result of Sample Steel C.
Figure 4 is a graph illustrating how an amount of residual ferrite varies depending on a heat treatment time at 800°C.
Figure 5A is a metal structure image of Sample Steel A after subjected to a heat treatment at 800°C for 30 minutes.
Figure 5B is a metal structure image of Sample Steel B after subjected to a heat treatment at 800°C for 30 minutes.
Figure 5C is a metal structure image of Sample Steel C after subjected to a heat treatment at 800°C for 30 minutes.
Figure 6 is a graph illustrating measurement results of a Charpy impact value as-dissolved and after subjected to a heat treatment at 800°C for 5 minutes.
Figure 7A is an electron photomicrograph of Sample Steel A as a comparative steel.
Figure 7B is a graph illustrating measurement results of concentration distributions of respective elements at an analysis position (along an analysis line) in an arrow direction in Fig. 7A.
Figure 7C is an electron photomicrograph of Sample Steel C as a steel useful to understand the present invention.
Figure 7D is a graph illustrating measurement results of concentration distributions of respective elements at an analysis position (along an analysis line) in an arrow direction in Fig. 7C.
Figure 8 is a graph illustrating comparison results in residual stress between before and after a heat treatment.
Figure 9 is a graph illustrating a comparison in Charpy impact test results between before and after the heat treatment.
Figure 10 is a graph illustrating a comparison in pitting potential among the steels.
Figure 11 is a cross-sectional view illustrating a vertical mixed flow seawater pump.
Figure 12 is a cross-sectional view illustrating a flow rate adjusting device.

Description of Embodiments and Examples useful to understand the Invention

[0015] The present invention relates to duplex stainless steels and structures using them. More specifically, the present invention relates to duplex stainless steels actually providing still better embrittlement resistance and productivity while maintaining good corrosion resistance by suppressing the formation of embrittlement phases; and products using the duplex stainless steels. The embrittlement phases are formed upon manufacturing (upon casting, forging, hot rolling, or welding), upon welding, and upon a heat treatment of highly corrosion-resistant duplex stainless steels and are exemplified by precipitates such as nitrides and carbides; and intermetallic compounds such as sigma phase and chi phase.

[0016] The present invention includes multiple aspects to achieve the object. For example, according to an embodiment of the present invention, tantalum (Ta) is positively added so as to suppress the intermetallic compound formation in a duplex stainless steel, because tantalum inhibits the diffusion or migration of intermetallic-compound-forming elements.

[0017] Specifically, the present invention provides a steel as set forth in claim 1.

[0018] Not to impair effects of the Ta addition, the stainless steel has a nitrogen content of 0.05% to 0.25% and a carbon content of 0.02% or less to suppress the formation of nitrides and carbides. The nitrogen content is preferably 0.05% to 0.19%.

[0019] The Si content is controlled to 0.5% or less, because Si accelerates the formation of intermetallic compounds and is not expected to be prevented from diffusing by Ta. From the viewpoint of corrosion resistance, the contents of elements that cause corrosion resistance are preferably adapted to be within a specific range. Accordingly, the stainless steel preferably has a pitting resistance equivalent number (PREW) of 40 or more, where the pitting resistance equivalent number PREW is specified by an expression given as follows:

$$\mathrm{PREW} = \%\mathrm{Cr} + 3.3 \times (\%\mathrm{Mo} + 0.5 \times \%\mathrm{W}) + 30 \times \%\mathrm{N}$$

where %Cr, %Mo, %W, and %N are contents (in mass percent) of Cr, Mo, W, and N, respectively.

[0020] Specifically, the present invention also provides, in an embodiment, a super duplex stainless steel containing, in mass percent, N in a content of 0.05% to 0.25%, C in a content of 0.02% or less, P in a content of 0.02% or less, Si in a content of 0.5% or less, Mn in a content of 1.2% or less, Ni in a content of 6.0% to 8.0%, Cr in a content of 24.0% to 26.0%, Mo in a content of 3.0% to 5.0%, W in a content of 4.0% or less, and Ta in a content of 0.2% to 0.5% and has a pitting resistance equivalent number (PREW) of 40 or more.

[0021] In yet another embodiment, the present invention provides a duplex stainless steel structure obtained by preparing a structure of an alloy having the chemical composition by forging or casting; and subjecting the formed structure to a solution heat treatment at a temperature of 950°C to 1200°C for a time period of 30 minutes to 2 hours so as to have a ratio of austenite phase to ferrite phase of 0.2 to 0.8. The resulting duplex stainless steel structure less suffers from embrittlement phase formation inside of the structure and can provide a product having good toughness.

[0022] Exemplary particularly useful structures formed from the alloy having the chemical compositions include marine structures; oil & gas structures (structures used in oil & gas environments); and pump impellers, pump casings, and flow rate adjusting devices for use in chemical plant structures.

[0023] Embodiments of the present invention and examples useful to understand it will be illustrated below with reference to the attached drawings.

[0024] The present inventors intended to help thick-walled cast products, forged products, and hot-worked products to have better productivity and embrittlement resistance while maintaining satisfactory corrosion resistance. Accordingly, they made investigations on technologies for suppressing embrittlement phase precipitation caused by intermetallic compounds and carbonitride. As a result, they had following findings.

[0025] Initially, an embrittlement phase formation mechanism of a customary sample containing no Ta will be illustrated.

[0026] Figure 1A is a conceptual diagram illustrating an embrittlement phase formation mechanism in a customary duplex stainless steel.

[0027] The duplex stainless steel in Fig. 1A includes a ferrite phase 1, an austenite phase 2, and a grain boundary 3 formed between the two phases. In the ferrite phase 1, an element that forms an intermetallic compound (intermetallic-compound-forming element 5) such as Cr, Mo, or W diffuses or migrates via a vacancy 4 and moves toward the grain boundary 3.

[0028] An intermetallic compound 6 and a carbide/nitride 7 (a carbide and/or a nitride) are formed in a grain boundary region including the grain boundary 3. These are also called embrittlement phases. A steel, if containing the embrittlement phases in large amounts, may become brittle and may often suffer from deterioration in corrosion resistance, embrittlement resistance, productivity, weldability, and thermal processability.

[0029] Next, an embrittlement phase formation suppressing mechanism in a tantalum-containing stainless steel according to the embodiment of the present invention will be illustrated.

[0030] Figure 1B is a conceptual diagram illustrating the embrittlement phase formation suppressing mechanism in the duplex stainless steel according to the present invention.

[0031] In the embodiment in Fig. 1B, a tantalum atom 11 occupies the vacancy 4 more readily than the intermetallic-compound-forming element 5 does and thereby inhibits the diffusion of the intermetallic-compound-forming element 5. This can prevent the formation typically of a nitride of the intermetallic-compound-forming element 5 in a grain boundary region 12.

[0032] The intermetallic compound 6 includes, for example, the sigma phase and chi phase and is known to be readily precipitated at the alpha phase-gamma phase interface as an origin and to grow toward the alpha phase. Cr, Mo, Si, and W each acting as an element forming the intermetallic compound 6 (intermetallic-compound-forming element 5) migrate from the metal matrix, are enriched at the grain boundary of the alpha phase/gamma phase interface and are precipitated as the intermetallic compound 6. The precipitation of the intermetallic compound 6 can be retarded probably by reducing the diffusion rate of the intermetallic-compound-forming elements 5. Of these elements, Cr, Mo, and W are over-size elements each having an atomic radius larger than the average atomic radius of elements forming the stainless steel and are considered to intensively interact with the atomic vacancy (vacancy 4) in the metal matrix and to move via the vacancy 4 as a preferential diffusion path.

[0033] It is therefore important to prevent the phenomenon and to inhibit the diffusion of the intermetallic-compound-forming elements 5. To this end, a specific element is added so as to allow the vacancy 4 to trap the added element, where the added element has an atomic radius larger than those of the intermetallic-compound-forming elements and interacts with the vacancy 4 more intensively than the elements do. This can reduce the diffusion rate of the intermetallic-compound-forming elements 5 particularly in a temperature range of 650°C to 950°C where embrittlement phase precipitation is an issue. Embrittlement in the temperature range can be avoided by rapid cooling in the case of a small-sized stainless steel (steel), but becomes an issue in the case of a large-sized steel because it is difficult to rapidly cool the inside of such large-sized steel. The present invention, in an embodiment, solves the problem by adapting the steel chemical composition.

[0034] Several elements having a large atomic radius may be listed as candidates to be added. In general, a metal element having a large atomic radius has an extremely low free energy to form a nitride or carbide.

[0035] A thermal equilibrium calculation demonstrates the following phenomena:
A nitride is formed in a liquid phase during manufacturing and is hardly dissolved in the matrix when Zr, Ti, Hf, or another element having a high nitride/carbide forming capability is added, particularly when the steel is a super duplex stainless steel added with nitrogen so as to have better corrosion resistance. Of elements having a relatively low nitride forming capability, niobium (Nb) is considered to be an element that is readily taken in the sigma phase that acts as an intermetallic compound by itself.

[0036] Based on the findings and considerations, tantalum (Ta) is selected as an element to be added, because Ta can be relatively easily dissolved in the metal matrix upon manufacturing and is resistant to precipitation as an intermetallic compound.

[0037] The roles of alloy elements to be added to the duplex stainless steel disclosed herein, and reasons why the chemical composition ranges are specified will be described below.

Chromium (Cr) content: 20.0% to 40.0%

[0038] Chromium element is a basic element and is most important in helping the stainless steel to maintain corrosion resistance at certain level. The stainless steel herein has to have a two-phase structure including both austenite and ferrite, as being a duplex stainless steel. For this reason, the chromium content is specified to be 20% or more in consideration of a chromium equivalent (Cr_{eq}) and a nickel equivalent (Ni_{eq}) as defined by expressions as follows; and a percentage (fraction) of the ferrite phase determined by these equivalents. The upper limit of the chromium content is specified to be 40% in consideration of economic efficiency, because increase in Cr_{eq} requires increase in Ni_{eq}. The chromium content is more preferably in the range of 24% to 26%.

$$Cr_{eq}=\%Cr+2\%Si+1.5\%Mo+0.75\%W+5\%V+5.5\%Al+1.75\%Nb+1.5\%Ti$$

$$Ni_{eq}=\%Ni+0.5\%Mn+30\%C+0.3\%Cu+25\%N+\%Co$$

where %Cr, %Si, %Mo, %W, %V, %Al, %Nb, %Ti, %Ni, %Mn, %C, %Cu , %N, and %Co are contents (in mass percent) of the respective elements.

$$\text{Ferrite phase fraction (in volume percent)} = 55 \times (Cr_{eq}/Ni_{eq}) - 66.1$$

Nickel (Ni) content: 3.0% to 12.0%

[0039] Nickel element stabilizes austenite and is useful in increasing general corrosion resistance in relation to corrosion resistance. The nickel content is therefore specified to be 3% or more. The nickel content is specified to be 12% or less in terms of upper limit in consideration of the relationship between the chromium equivalent and the nickel equivalent, the phase fraction, and the economic efficiency. The nickel content is more preferably in the range of 6% to 8%.

Molybdenum (Mo) content: 7.0% or less

[0040] Molybdenum element is important in helping the stainless steel to maintain corrosion resistance as with chromium, functionally stabilizes the ferrite phase, but may accelerate the intermetallic compound formation, when it is added. To prevent this, the molybdenum content is controlled to 7.0% or less. The molybdenum content is more preferably in the range of 3.0% to 5.0%.

Tungsten (W) content: 6.5% or less

[0041] Tungsten element improves the corrosion resistance. A precipitation rate of intermetallic compounds is reduced by replacing tungsten with Mo in a half amount, and thereby improves the corrosion resistance and mechanical properties. Tungsten, however, is an expensive alloy element. And tungsten may accelerate the intermetallic compound formation and adversely affect the corrosion resistance of a weld bead when it is added in a large amount. To prevent this, the tungsten content is controlled to 6.5% or less. The tungsten content is more preferably in the range of 4.0% or less.

Silicon (Si) content: 3.0% or less

[0042] Silicon element stabilizes the ferrite phase and is effective for deoxidation during manufacturing. The element also increases the fluidity of a molten steel upon manufacturing and welding and thereby reduces surface defects. The element, however, increases the precipitation rate of intermetallic compounds and reduces the steel ductility. To prevent this, the silicon content is preferably 3.0% or less and more preferably 0.5% or less.

Manganese (Mn) content: 8.0% or less

[0043] Manganese stabilizes austenite, can act as an alternative to expensive nickel, increases the nitrogen solid solubility, and increases deformation resistance at a high temperature. Manganese added in an appropriate amount is necessary particularly when nitrogen is positively added so as to offer better corrosion resistance. The element has a deoxidation effect upon melting and refining, but may cause the stainless steel to have inferior corrosion resistance and may accelerate the formation of intermetallic compounds, when it is added in an excessively large amount. To prevent this, the manganese content is preferably controlled to 8% or less in terms of its upper limit. The manganese content is more preferably in the range of 1.2% or less.

Nitrogen (N) content: 0.7% or less

[0044] Nitrogen element is useful for improving the resistance to pitting corrosion and is one of most important elements in relation to corrosion resistance, because nitrogen has the effect in a magnitude of about 30 times that of chromium. When the carbon content is reduced to prevent grain boundary sensitization, nitrogen is added to compensate the strength of the steel. However, nitrogen may cause cracking due to blowhole generation during manufacturing if it is added in a content greater than 0.7%. To prevent this, the nitrogen content is preferably controlled to 0.7% or less. Nitrogen forms Ta-containing nitrides and impairs the effects of Ta addition when nitrogen is present in combination with Ta as added. To prevent this and to allow nitrogen to dissolve in the alpha phase and gamma phase in a good balance without causing loss of corrosion resistance, the nitrogen content is more preferably 0.3% or less, furthermore preferably 0.05% to 0.25%, and particularly preferably in the range of 0.05% to 0.19%.

Carbon (C) content: 0.1% or less

[0045] Carbon element forms carbides and induces grain boundary sensitization upon welding. Carbon forms Ta-containing carbides and impairs the effects of Ta addition when carbon is present in combination with Ta as added. To prevent this, the carbon content is preferably minimized. However, reduction in the carbon content may invite increase in production cost. The carbon content is therefore specified to 0.1% or less. The carbon content is more preferably in the range of 0.02% or less.

Tantalum (Ta) content: 0.05% to 1.0%

[0046] Tantalum element is one of elements featuring the present invention. Tantalum has an atomic radius larger than the average atomic radius of elements forming the duplex stainless steel, advantageously prevents the diffusion of major intermetallic-compound-forming elements, and effectively reduces the precipitation rate of intermetallic compounds, as is described above. However, tantalum invites poor economy, and further disturbs the balance in ratio between the ferrite phase and austenite phase, if tantalum is added in an excessively high content. To prevent this, the tantalum content is preferably controlled to 1.0% in terms of its upper limit. In contrast, if tantalum is added in a content less than 0.05%, its effects may be not expected. The tantalum content is more preferably in the range of 0.2% to 0.5% in view of the balance in the amount of Ta to form a solid solution in the nitride phase and the ferrite phase.

Phosphorus (P) content: 0.1% or less

[0047] Phosphorus element is an impurity inevitably contaminated into the steel. The element impairs the corrosion resistance, segregates at the grain boundary, and thereby accelerates the embrittlement phase precipitation. To prevent this, the phosphorus content is preferably minimized and is controlled preferably to 0.1% or less, more preferably to 0.02% or less, and particularly preferably to 0.005% or less. Excessive reduction in phosphorus content, however, may invite increase in production cost. The phosphorus content may be determined also in this view.

[0048] The present invention will be further illustrated with reference to the examples below which are an example useful to understand the invention and comparative examples.

Examples

[0049] Table 1 indicates chemical compositions (in mass percent) of duplex stainless steels according to Example 1 example useful to understand the invention (Sample Steel C)) and Comparative Examples 1 and 2 (comparative steels (Sample Steels A and B)).

[0050] These material steels were each subjected to a heat treatment and were compared, where the heat treatment simulated cooling upon manufacturing and reheating by welding.

[0051] Ingots of duplex stainless steels having chemical compositions given in Table 1 were made in a vacuum melting furnace each in an amount of 20 kg. Sample Steel A had a chemical composition equivalent to that of a standardized steel S32750. Sample Steel B had a chemical composition having low N, C, and Si contents. Sample Steel C had a chemical composition of an alloy equivalent to Sample Steel B, except for being added with a very small amount of Ta.

[Table 1]

[0052]

TABLE 1

*1: PREW=Cr+3.3(Mo+0.5W)+30N (in mass percent)

Symbol	Material	Chemical composition (in mass percent)														PREW*1
		Basic element								Added element	Impurity					
		Fe	C	Cr	Ni	Mo	N	Mn	Cu	Ta	P	S	Si	O	Al	
A	Comparative Example 1	bal.	0.024	25.28	7.01	3.90	0.27	0.99	0.43	-	0.017	0.0021	0.57	0.0034	0.055	46.25
B	Comparative Example 2	bal.	0.0100	25.14	6.96	3.92	0.18	0.97	0.41	-	0.006	0.0017	0.02	0.0088	0.011	43.48
C	Example 1	bal.	0.0107	25.04	7.00	3.97	0.18	0.98	0.41	0.37	0.003	0.0019	0.02	0.0049	0.03	43.54

[0053] The ingots were heated to 1250°C, forged, and yielded steel plates of 20 by 50 by 150 (mm). The forged steel plates were each subjected to a solution heat treatment at 1100°C for one hour so as to give an appropriate ratio of austenite phase to ferrite phase; and then rapidly cooled by water cooling so as to avoid embrittlement phase precipitation.

[0054] Figures 2A, 2B and 2C depict external view images of Sample Steels A, B and C prepared by forging, respectively.

[0055] The images demonstrate that the sample steels could be manufactured without suffering from cracking and defects due to forging.

[0056] Figures 3A, 3B and 3C depict metal structure observation results of Sample Steels A, B and C after manufacturing, respectively.

[0057] The metal structure observation was performed so that each sample steel was polished with SiC abrasive papers to #2000, subjected to finish polishing with 1-μm diamond abrasive grains, and electrolytically etched with a 10% sodium hydroxide (NaOH) aqueous solution. This process colored a ferrite phase 31 brown; and intermetallic compounds, carbides, and nitrides black. An austenite phase 32 appeared white.

[0058] Each test specimen was observed with an optical microscope after being subjected to ultrasonic cleaning with acetone and distilled water. Metal structure observations as mentioned later were performed by the above procedure. The results of metal structure observations in Figures 3A, 3B and 3C demonstrate that each sample steel had a two-phase structure including both ferrite and austenite phases clearly distinguishable from each other.

[0059] The sample steels were each subjected to a heat treatment at 800°C, where the temperature is within a temperature range in which an embrittlement phase is readily precipitated. This was performed so as to evaluate the embrittlement phase precipitation under conditions of cooling during manufacturing and of reheating by welding.

[0060] Figure 4 is a graph illustrating how the amount of residual ferrite varies depending on the heat treatment time at 800°C. The graph is plotted with the abscissa indicating the heat treatment time and the ordinate indicating the ferrite amount. The ferrite amount was measured with a ferrite scope using magnetic induction. The tendency of intermetallic compound precipitation can be evaluated by evaluating the amount of residual ferrite. This is because the intermetallic compound precipitation which is one of embrittlement phase precipitations proceeds as a result of decomposition of the ferrite phase into an intermetallic compound phase and an austenite phase under a precipitation temperature condition.

[0061] Figure 4 demonstrates that the stainless steel of Example 1 had a lower rate of ferrite phase decrease and less suffered from the decomposition of the ferrite phase than those of Comparative Examples 1 and 2.

[0062] Figure 5A, 5B and 5C depict metal structure images of Sample Steel A, B and C, respectively, after a heat treatment at 800°C for 30 minutes.

[0063] The figures demonstrate that an embrittlement phase 53 increased in addition to a ferrite phase 51 and an austenite phase 52.

[0064] The figures demonstrate that Sample Steel C (Example) included the embrittlement phase 53 as precipitated in a smaller amount than those of Sample Steels A and B as the comparative steels (Comparative Examples) and less suffered from the precipitation of the embrittlement phase 53. Among the comparative steels, Sample Steel B included the embrittlement phase 53 in a larger amount.

[0065] Figure 6 depicts Charpy impact value measurement results after a heat treatment at 800°C for 5 minutes.

[0066] The Charpy impact value was measured according to Japanese Industrial Standard (JIS) Z2242 (2005). The measurement was performed by a procedure schematically illustrated as follows.

[0067] Charpy test specimens having a size of 10 mm by 10 mm by 55 mm and having a 2-mm V-notch were sampled from each sample steel plate before and after the heat treatment from the longitudinal direction of the plate so that the central part should be the notched portion, and impact values of the test specimens were measured.

[0068] Figure 6 demonstrates that Sample Steel C had a Charpy impact value after the heat treatment of higher than those of Sample Steels A and B as the comparative steels. This indicates that the suppression of intermetallic compound formation helped the steel to have better toughness.

[0069] Figures 7A, 7B, 7C and 7D depict energy-dispersive X-ray (EDX) analyses results at a grain boundary (alpha/gamma interface) after a heat treatment at 800°C for one minute.

[0070] Figures 7A and 7B depict an electron photomicrograph and measurement results of concentration distributions of respective elements at the analysis position (along the analysis line) in the arrow direction in Fig. 7A, respectively, of Sample Steel A as the comparative steel.

[0071] Figures 7C and 7D depict an electron photomicrograph and measurement results of concentration distributions of respective elements at the analysis position (along the analysis line) in the arrow direction in Fig. 7C, respectively, of Sample Steel C.

[0072] Figures 7A and 7C depict fine structures of a ferrite phase 71 and an austenite phase 72 clearly, with a grain boundary indicated by dashed lines. The concentrations of respective elements were measured at the analysis position 73 indicated by the line in the arrow direction (from the austenite phase 72 to the ferrite phase 71).

[0073] Figures 7B and 7D are plotted with the abscissa indicating the distance and the ordinate indicating the concentration.

[0074] With reference to Fig. 7B, the comparative steel had high Mo and Cr concentrations in the vicinity of the grain boundary facing the ferrite phase.

[0075] In contrast, with reference to Fig. 7D, the sample steel C had a Ta concentration peak in the vicinity of the grain boundary facing the ferrite phase and exhibited lower Mo and Cr concentrations than those of the comparative steel in Fig. 7B.

[0076] In other words, tantalum (Ta) preferably diffuses at the ferrite-austenite grain boundary and thereby inhibits the diffusion of Mo and Cr acting as intermetallic-compound-forming elements.

[0077] The results demonstrate that Ta diffused to the grain boundary by itself, thereby inhibited the diffusion of intermetallic-compound-forming elements such as Mo and Cr, and reduced or retarded the formation of the intermetallic compounds, when Ta is added.

[Effects of Heat Treatment on Residual Stress and Impact Value]

[0078] The sample steel C and comparative steels were each subjected to a heat treatment simulating a post weld heat treatment (PWHT) for residual stress relaxation, and how the heat treatment affects the residual stress and impact value was evaluated.

[0079] A tensile residual stress was applied to each of Sample Steels A, B and C by subjecting them to surface grinding of the steel plate using a grindstone with a grain size of #46 at a rotation speed of 1440 rpm to a depth of cut of 0.01 mm and thereby imparting a highly deformed layer to the surface. The test samples each applied with the residual stress in the surface by surface grinding were subjected to a heat treatment at 650°C for 30 minutes simulating the PWHT, and how the heat treatment conditions affect the residual stress and mechanical properties was evaluated.

[0080] Figure 8 depicts results of comparisons in residual stress between before and after the heat treatment. The residual stress values were measured for the ferrite phase and for the austenite phase, respectively. The measured values were multiplied by the volume ratio of each phase and averaged, and the average was defined as a macro-stress and evaluated.

[0081] Each of the test samples was imparted with a tensile stress of about 900 to about 1100 MPa by the surface processing (surface grinding), but had a lower tensile stress of about 200 MPa after the heat treatment at 650°C for 30 minutes, indicating that the heat treatment gave a stress relaxation effect of about eight-tenths the initial stress.

[0082] Figure 9 depicts comparison results in the Charpy impact test between before and after the heat treatment.

[0083] Figure 9 demonstrates that the sample steel C had a better impact value than those of the comparative steels and maintained an impact value of about 100 J/cm^2 even after the heat treatment. Specifically, the sample steel C maintained an impact value of 100 J/cm^2 or more even after the heat treatment at 650°C for 30 minutes, where the heat treatment relaxed the residual stress by eight-tenths the initial stress.

[Effects of Heat Treatment on Pitting Potential]

[0084] A pitting potentials was measured before and after the heat treatment (at 650°C for 30 minutes), and the results are indicated below.

[0085] The pitting potential was measured according to JIS G0577 (2005).

[0086] Figure 10 depicts a comparison in pitting potential among the sample steel C and the comparative steels.

[0087] Figure 10 demonstrates that the order of pitting corrosion resistance (after the heat treatment) of the respective sample steels is as follows.

[0088] Sample Steel C > Sample Steel B (comparative steel) > Sample Steel A (comparative steel; corresponding to customary steel S32750).

[0089] Specifically, the sample steel C had a pitting potential higher than that of the customary steel.

[0090] The results demonstrate that the sample steel C had pitting corrosion resistance equal to or higher than that of the customary steel even though the sample steel C became more resistant to embrittlement.

[Product 1 Using Sample Steel C]

[0091] Figure 11 is a cross-sectional view of a vertical mixed flow seawater pump.

[0092] The vertical mixed flow seawater pump in Fig. 11 includes components such as a bell mouth 117 that reduces the drag of seawater coming in from a feed channel; a shaft 111 that transfers the rotative power of a driving motor; an impeller hub 115 that is fixed to the shaft 111; impeller vanes 113 that impart the rotative power of the driving motor to the seawater efficiently; a casing liner 114 that has a spherical inner wall so as to allow the impeller vanes 113 to have an always constant outer clearance; a casing 112 that converts the velocity energy of the seawater given by the impeller vanes 113 into pressure energy; a column pipe 119 that allows the pressurized seawater to pass therethrough; an impeller cap 116; and a cone 118.

[0093] The casing liner 114 and the casing 112 were each formed from the steel of Example 1 by casting; whereas the impeller hub 115 and the impeller vanes 113 were each formed from the steel of Example 1 by forging. These steels after casting or forging were subjected to a solution heat treatment at 1100°C for one hour and then subjected to water cooling so as to have a two-phase composition including ferrite in an amount of 40% to 50% to give the structures. A junction between the casing liner 114 and the casing 112 and junctions between the impeller hub 115 and the impeller vanes 113 were bonded by metal inert gas arc welding (MIG welding). Weld heat affected zones were wrapped around with a band heater, heated up to 650°C, and subjected to a heat treatment at that temperature (650°C) for 30 minutes, followed by rapid cooling.

[0094] The residual stress of the weld heat affected zones was measured by X-ray residual stress measurement to find that the tensile stress was reduced down to 80 MPa. The steel of Example 1, as used, enabled the manufacturing of a seawater pump that less suffered from reduction in weld toughness, had a higher fatigue strength (better fatigue resistance), and had a longer working life.

[Product 2 Using sample steel C]

[0095] Figure 12 is a cross-sectional view of a flow rate adjusting device.

[0096] The flow rate adjusting device in Fig. 12 includes components such as a casing 121 that supports the entire device; a valve element 122 that controls a flow rate; a valve seat 123 into which the valve element 122 is fit; a handle 125; and a shaft 124 that controls the position of the valve element 122 by the rotation of the handle 125.

[0097] The casing 121 was formed from the steel of Example 1 by casting. The steel of Example 1 enabled the manufacturing of a large-sized flow rate adjusting device having satisfactory corrosion resistance, as used.

[0098] The flow rate adjusting device is usable in environments typically of seawater, petroleum, and chemical plants.

Reference Signs List

[0099] 1...ferrite phase, 2...austenite phase, 3...grain boundary, 4...vacancy, 5...intermetallic-compound-forming element, 6...intermetallic compound, 7... carbide/nitride, 11...tantalum atom, 12...grain boundary region, 31, 51, 71...ferrite phase, 32, 52, 72...austenite phase, 53...embrittlement phase, 73...analysis position, 111...shaft, 112 ... casing, 113... impeller vane, 114...casing liner, 115...impeller hub, 116...impeller cap, 117...bell mouth, 118...cone, 119...column pipe, 121...casing, 122...valve element, 123...valve seat, 124...shaft, 125...handle.

Claims

1. A duplex stainless steel consisting of:

N in a content of 0.05% to 0.25%;
C in a content of 0.02% or less;
P in a content of 0.02% or less;
Si in a content of 0.5% or less;
Mn in a content of 1.2% or less;
Ni in a content of 6.0% to 8.0%;
Cr in a content of 24.0% to 26.0%;
Mo in a content of 3.0% to 5.0%;
W in a content of 6.5% or less; and
Ta in a content of 0.2% to 0.5%, in mass percent,
with the remainder being Fe and inevitable impurities.

2. The duplex stainless steel according to claim 1, wherein the duplex stainless steel has a pitting resistance equivalent number (PREW) of 40 or more as specified by an expression given as follows:

$$\mathrm{PREW} = \%\mathrm{Cr} + 3.3 \times (\%\mathrm{Mo} + 0.5 \times \%\mathrm{W}) + 30 \times \%\mathrm{N}$$

where %Cr, %Mo, %W and %N are contents in mass percent of Cr, Mo, W and N, respectively.

3. A duplex stainless steel structure using the duplex stainless steel of one of claims 1 and 2.

4. A method of obtaining a duplex stainless steel structure by:

   forming a structure from a duplex stainless steel in accordance with any of claims 1 and 2 by one of forging and casting; and
   subjecting the formed structure to a solution heat treatment at a temperature of 950°C to 1200°C for a time period of 30 minutes to 2 hours so as to have a ratio of austenite phase to ferrite phase of 0.2 to 0.8.

5. A marine structure as the duplex stainless steel structure of claim 3.

6. An oil & gas structure as the duplex stainless steel structure of claim 3.

7. A pump impeller as the duplex stainless steel structure of claim 3.

8. A pump casing as the duplex stainless steel structure of claim 3.

9. A valve element of a flow rate adjusting device, as the duplex stainless steel structure of claim 3.

Patentansprüche

1. Duplex-Edelstahl, in Massenprozent bestehend aus:

   N in einem Gehalt von 0,05% bis 0,25%;
   C in einem Gehalt von 0,02% oder weniger;
   P in einem Gehalt von 0,02% oder weniger;
   Si in einem Gehalt von 0,5% oder weniger;
   Mn in einem Gehalt von 1,2% oder weniger;
   Ni in einem Gehalt von 6,0% bis 8,0%;
   Cr in einem Gehalt von 24,0% bis 26,0%;
   Mo in einem Gehalt von 3,0% bis 5,0%;
   W in einem Gehalt von 6,5% oder weniger; und
   Ta in einem Gehalt von 0,2% bis 0,5%,
   wobei der Rest Fe und unvermeidbare Verunreinigungen ist.

2. Duplex-Edelstahl nach Anspruch 1, der eine durch den im Folgenden wiedergegebenen Ausdruck festgelegte Lochfraß-Widerstandsfähigkeits-Äquivalenzzahl (PREW) von 40 oder mehr aufweist:

$$\mathrm{PREW} = \%\mathrm{Cr} + 3{,}3 \times (\%\mathrm{Mo} + 0{,}5 \times \%\mathrm{W}) + 30 \times \%\mathrm{N}$$

   wobei %Cr, %Mo, %W und %N entsprechenderweise die Gehalte von Cr, Mo, W and N in Massenprozent sind.

3. Duplex-Edelstahlstruktur unter Verwendung des Duplex-Edelstahls nach einem der Ansprüche 1 und 2.

4. Verfahren zur Gewinnung einer Duplex-Edelstahlstruktur, indem:

   durch Schmieden oder Gießen eine Struktur aus einem Duplex-Edelstahl nach einem der Ansprüche 1 und 2 gebildet wird; und
   die gebildete Struktur einer Lösungs-Wärmebehandlung bei einer Temperatur von 950°C bis 1200°C über eine Zeitspanne von 30 Minuten bis 2 Stunden ausgesetzt wird, sodass sie ein Verhältnis der Austenit-Phase zur Ferrit-Phase von 0,2 bis 0,8 aufweist.

5. Seetechnische Struktur, die eine Duplex-Edelstahlstruktur nach Anspruch 3 darstellt.

6. Öl- und gastechnische Struktur, die eine Duplex-Edelstahlstruktur nach Anspruch 3 darstellt.

7. Pumpenflügelrad, das eine Duplex-Edelstahlstruktur nach Anspruch 3 darstellt.

8. Pumpengehäuse, das eine Duplex-Edelstahlstruktur nach Anspruch 3 darstellt.

9. Ventilelement einer Strömungsraten-Einstellvorrichtung, das eine Duplex-Edelstahlstruktur nach Anspruch 3 darstellt.

Revendications

1. Acier inoxydable duplex consistant en :

N à une teneur de 0,05% à 0,25% ;
C à une teneur de 0,02% ou moins ;
P à une teneur de 0,02% ou moins ;
Si à une teneur de 0,5% ou moins ;
Mn à une teneur de 1,2% ou moins ;
Ni à une teneur de 6,0% à 8,0% ;
Cr à une teneur de 24,0% à 26,0% ;
Mo à une teneur de 3,0% à 5,0% ;
W à une teneur de 6,5% ou moins ; et
Ta à une teneur de 0,2% à 0,5%,
en pourcentage en masse,
avec le reste étant Fe et des impuretés inévitables.

2. Acier inoxydable duplex selon la revendication 1, dans lequel l'acier inoxydable duplex a un nombre équivalent de résistance à la piqûration (PREW) de 40 ou plus tel que spécifié par une expression donnée comme suit :

$$\text{PREW} = \%\text{Cr}+3{,}3\text{x}(\%\text{Mo}+0{,}5\text{x}\%\text{W})+30\text{x}\%\text{N}$$

où %Cr, %Mo, %W et %N sont des teneurs en pourcentage en masse de Cr, Mo, W et N, respectivement.

3. Structure en acier inoxydable duplex utilisant l'acier inoxydable duplex selon l'une des revendications 1 et 2.

4. Procédé d'obtention d'une structure en acier inoxydable duplex par :

formation d'une structure à partir d'un acier inoxydable duplex selon l'une quelconque des revendications 1 et 2 par un(e) d'un forgeage et d'une coulée ; et
soumission de la structure formée à un traitement thermique de mise en solution à une température de 950°C à 1 200°C sur une période de temps de 30 minutes à 2 heures de manière à avoir un rapport de la phase austénitique sur la phase ferritique de 0,2 à 0,8.

5. Structure marine comme la structure en acier inoxydable duplex selon la revendication 3.

6. Structure pour pétrole et gaz comme la structure en acier inoxydable duplex selon la revendication 3.

7. Rotor de pompe comme la structure en acier inoxydable duplex selon la revendication 3.

8. Corps de pompe comme la structure en acier inoxydable duplex selon la revendication 3.

9. Élément de soupape d'un dispositif d'ajustement de débit, comme la structure en acier inoxydable duplex selon la revendication 3.

FIG. 1A

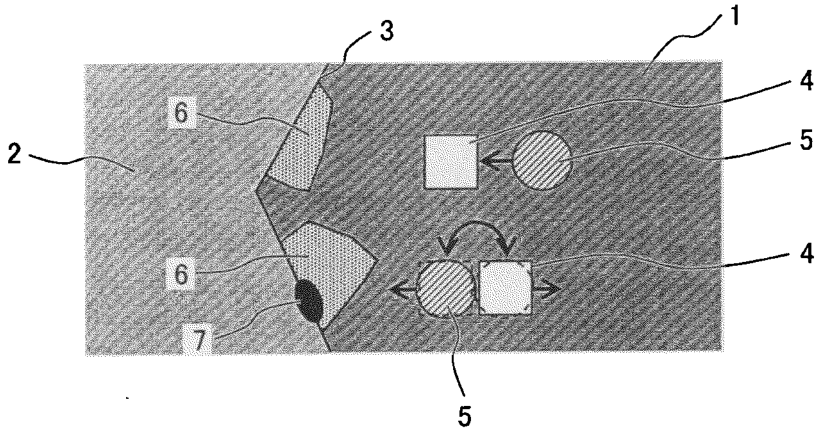


FIG. 1B

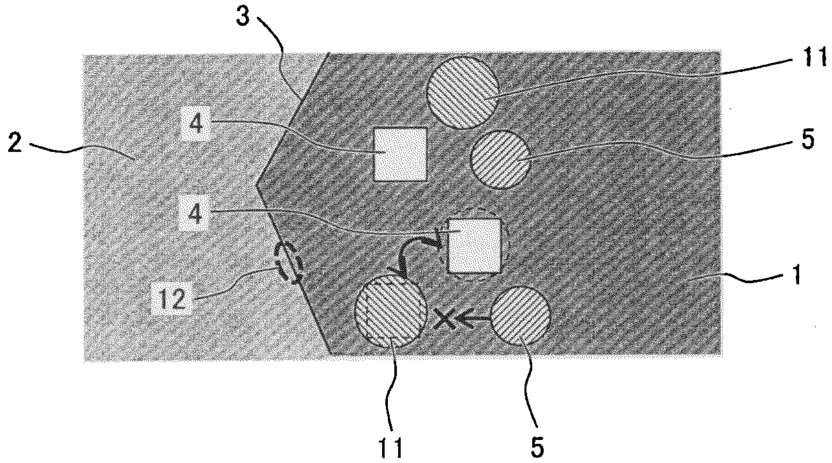


FIG. 2A

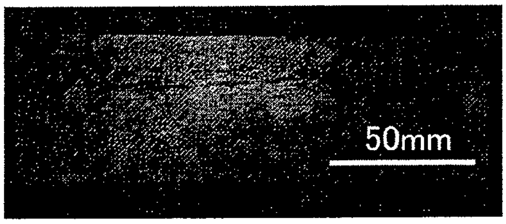


FIG. 2B

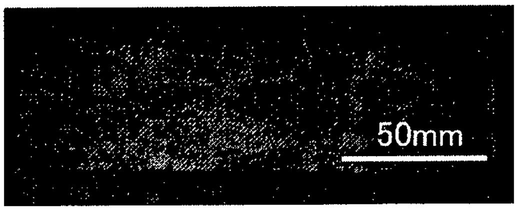


FIG. 2C

FIG. 3A

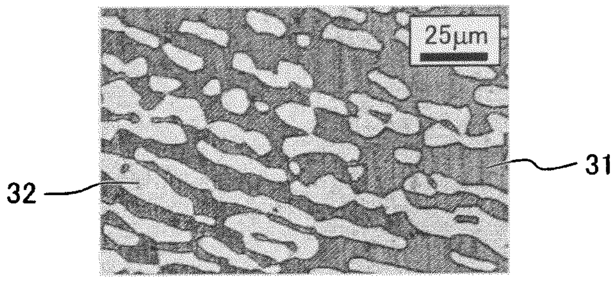


FIG. 3B

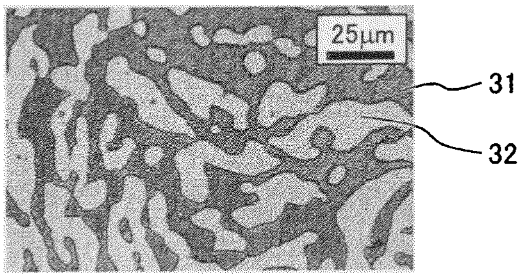


FIG. 3C

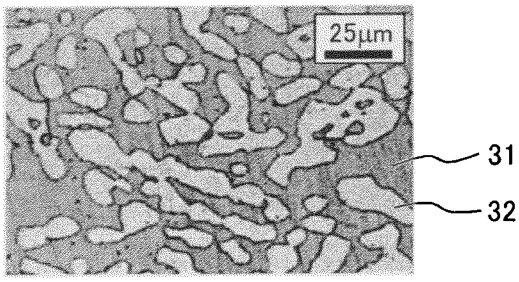


FIG. 4

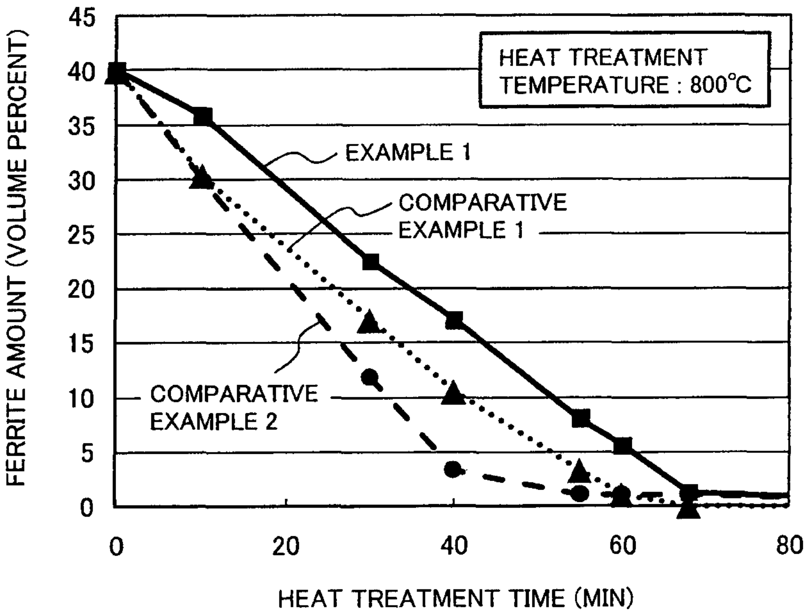

HEAT TREATMENT
TEMPERATURE : 800°C
EXAMPLE 1
COMPARATIVE
EXAMPLE 1
COMPARATIVE
EXAMPLE 2
FERRITE AMOUNT (VOLUME PERCENT)
45
40
35
30
25
20
15
10
5
0
0
20
40
60
80
HEAT TREATMENT TIME (MIN)

FIG. 5A

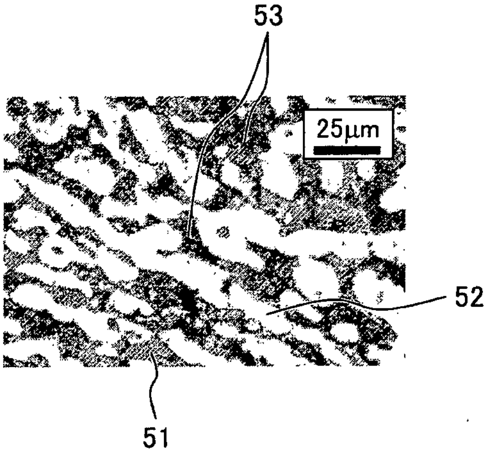


FIG. 5B

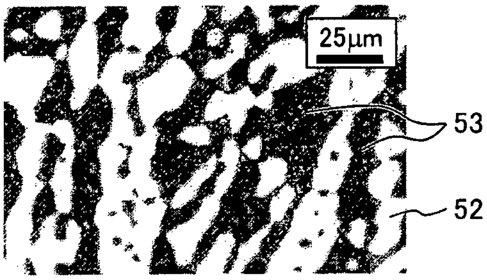


FIG. 5C

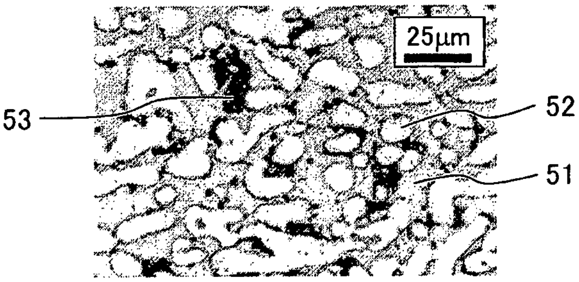


FIG. 6

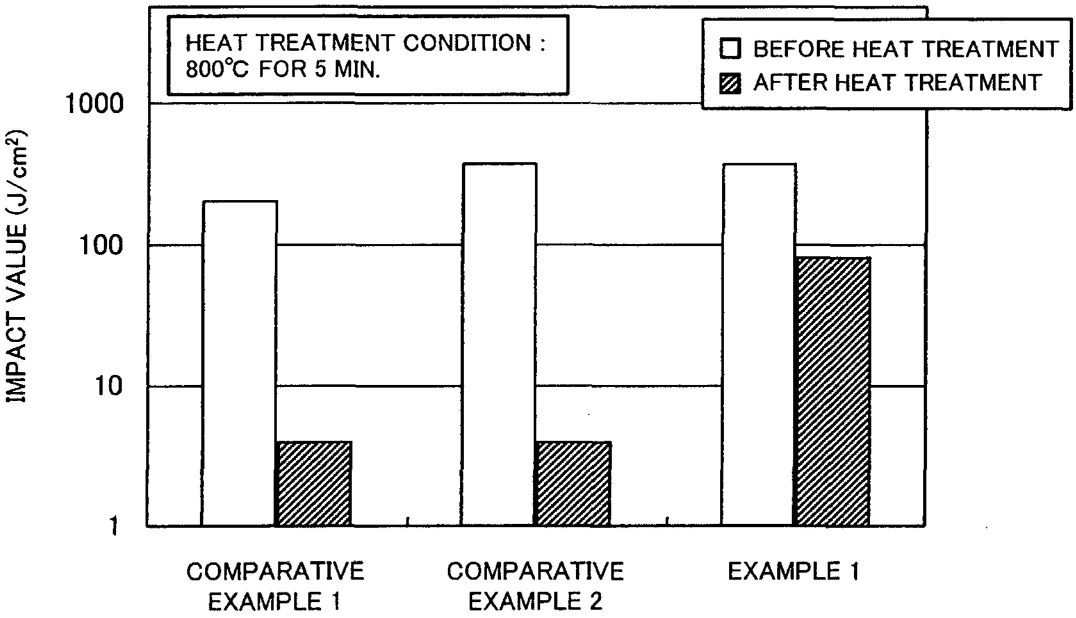

HEAT TREATMENT CONDITION :
800°C FOR 5 MIN.
☐ BEFORE HEAT TREATMENT
▨ AFTER HEAT TREATMENT
IMPACT VALUE (J/cm²)
1000
100
10
1
COMPARATIVE EXAMPLE 1
COMPARATIVE EXAMPLE 2
EXAMPLE 1

FIG. 7A

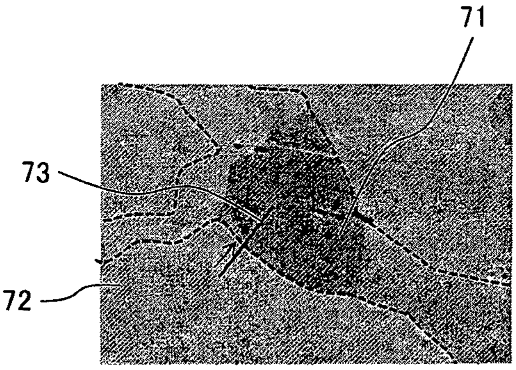

71
73
72

FIG. 7B

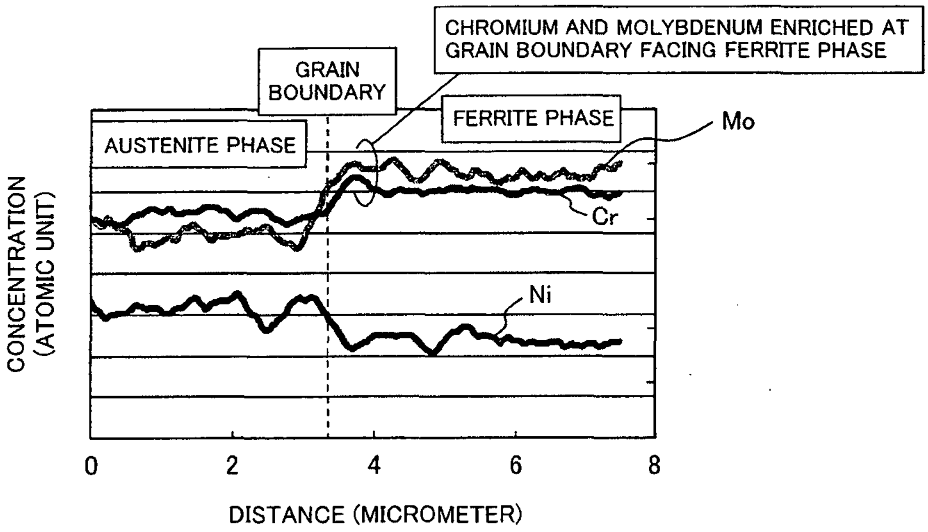

CHROMIUM AND MOLYBDENUM ENRICHED AT GRAIN BOUNDARY FACING FERRITE PHASE
GRAIN BOUNDARY
FERRITE PHASE
AUSTENITE PHASE
Mo
Cr
Ni
CONCENTRATION (ATOMIC UNIT)
0
2
4
6
8
DISTANCE (MICROMETER)

FIG. 7C

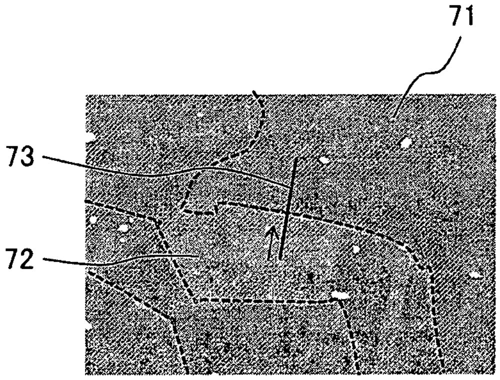

71
73
72

FIG. 7D

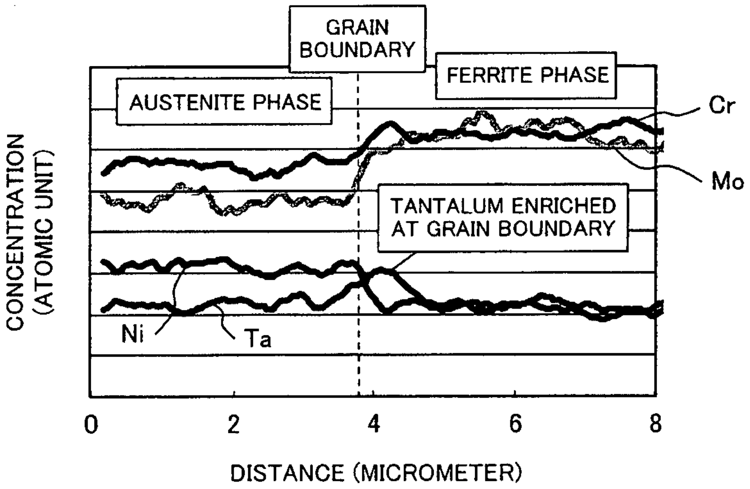

GRAIN BOUNDARY
AUSTENITE PHASE
FERRITE PHASE
Cr
Mo
TANTALUM ENRICHED AT GRAIN BOUNDARY
Ni
Ta
CONCENTRATION (ATOMIC UNIT)
0
2
4
6
8
DISTANCE (MICROMETER)

FIG. 8

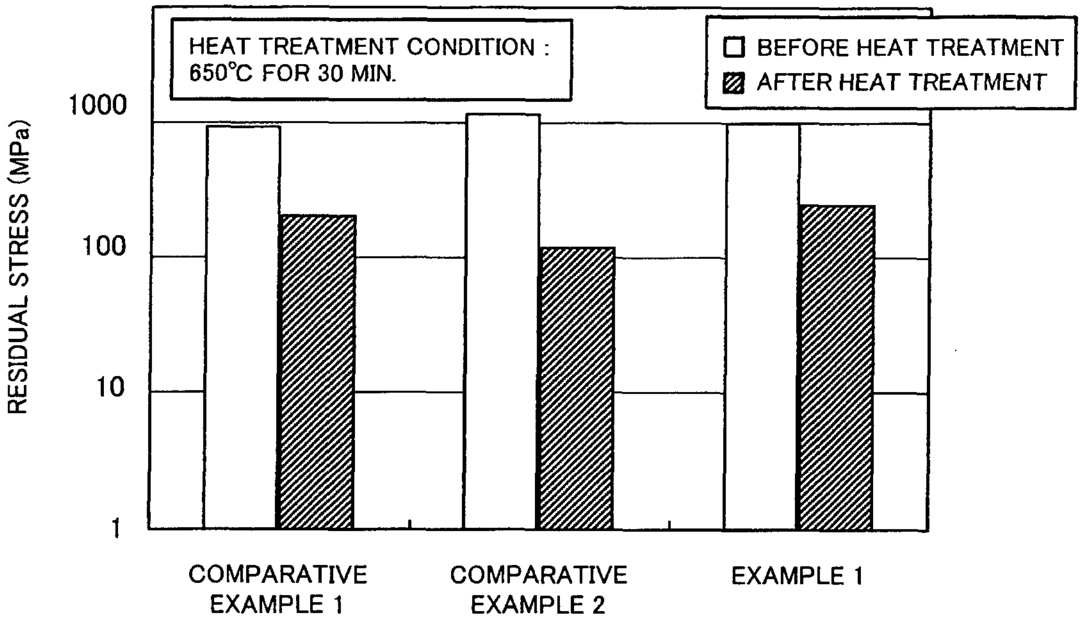

HEAT TREATMENT CONDITION :
650°C FOR 30 MIN.
☐ BEFORE HEAT TREATMENT
▨ AFTER HEAT TREATMENT
RESIDUAL STRESS (MPa)
1000
100
10
1
COMPARATIVE EXAMPLE 1
COMPARATIVE EXAMPLE 2
EXAMPLE 1

FIG. 9

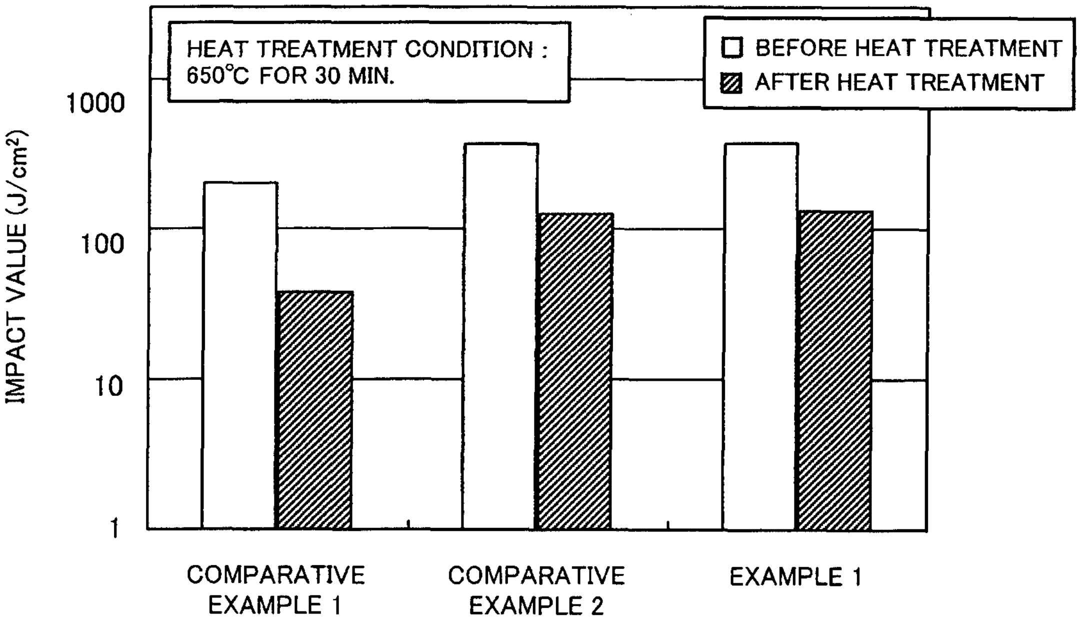

HEAT TREATMENT CONDITION :
650°C FOR 30 MIN.
☐ BEFORE HEAT TREATMENT
▨ AFTER HEAT TREATMENT
IMPACT VALUE (J/cm²)
1000
100
10
1
COMPARATIVE EXAMPLE 1
COMPARATIVE EXAMPLE 2
EXAMPLE 1

FIG. 10

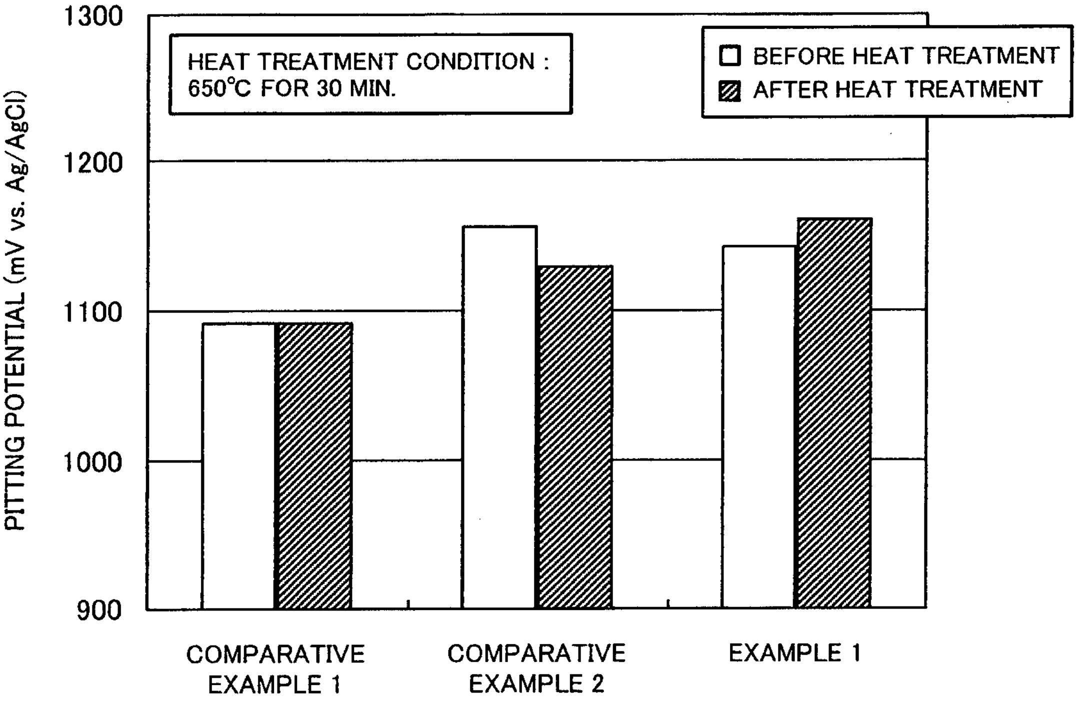

1300
1200
1100
1000
900
PITTING POTENTIAL (mV vs. Ag/AgCl)
HEAT TREATMENT CONDITION :
650°C FOR 30 MIN.
☐ BEFORE HEAT TREATMENT
▨ AFTER HEAT TREATMENT
COMPARATIVE EXAMPLE 1
COMPARATIVE EXAMPLE 2
EXAMPLE 1

FIG. 11

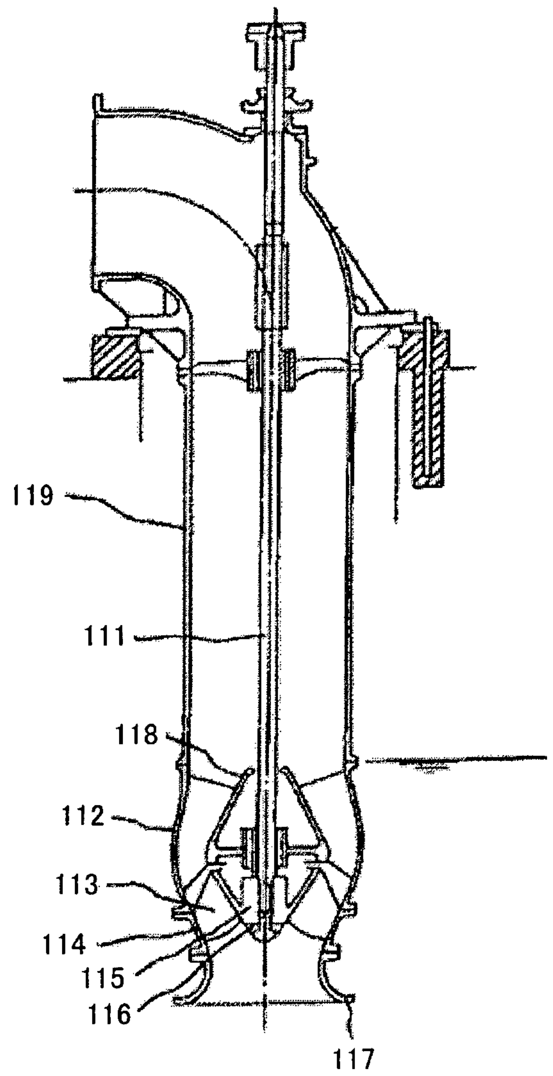
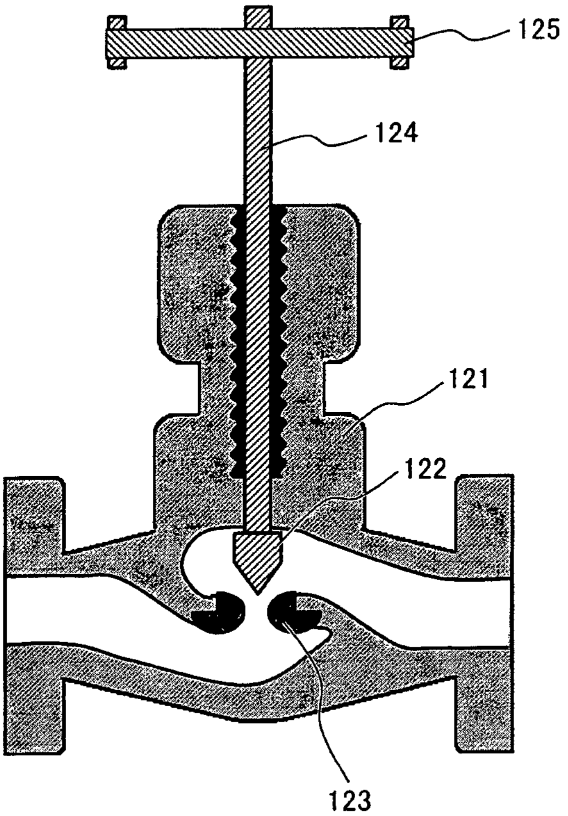


FIG. 12



REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- EP 0818552 A2 **[0008]**
- US 4055448 A **[0008]**
- JP 2011174183 A **[0009]**
- EP 1803832 A1 **[0009]**