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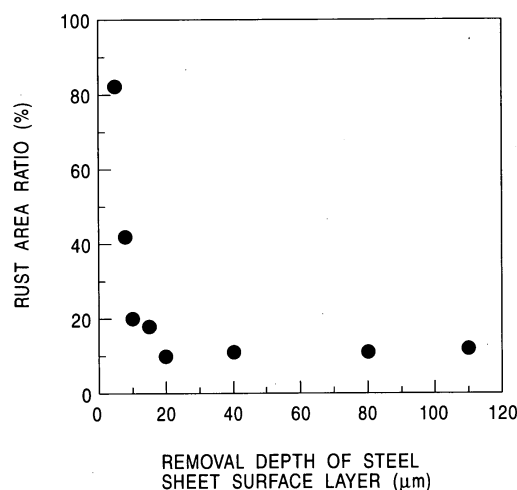
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(54) **Cr STEEL FOR STRUCTURAL USE AND METHOD FOR PRODUCING THE SAME**

(57) To provide structural Cr-containing steel with excellent low-temperature toughness and impact toughness, with low costs as compared with stainless steel, and with sufficient corrosion resistance. Specifically, this is structural Cr-containing steel and a manufacturing method thereof, wherein the Cr-containing steel contains C of 0.002 to 0.02%; N of 0.002 to 0.02%; Si of 0.05 to 1.0%; Mn of 0.05 to 1.0%; P of 0.04% or less; S of 0.02% or less; Al of 0.001 to 0.1%; and Cr of 6.0 to 10.0%, further may contain Cu of 0.1 to 1.0%, further may contain at least one of: Ni of 0.1 to 1.0%; and Mo of 0.1 to 1.0%, and further may contain at least one of: Nb of 0.005 to 0.10%; and V of 0.005 to 0.20%, the balance are formed of Fe and unavoidable impurities, and the Cr-concentration in the surface layer of the steel is equal to or more than the value wherein 1% is subtracted from the Cr-concentration within the steel.

FIG. 1



Description

Technical Field

[0001] The present invention relates to structural Cr-containing steel, particularly to Cr-containing steel employed for freezing containers with excellent low-temperature toughness and impact toughness, with low costs as compared with austenitic stainless steel, and with sufficient corrosion resistance.

Background Art

[0002] In recent years, demand for freezing containers is rapidly increasing along with improvement in the human diet. The performance required for the steel employed as a structural material for freezing containers, which are mainly used for long distance transport of provisions, includes high corrosion resistance, high low-temperature toughness, and that in the event that the structural material suffers impact the structural material is not readily punctured, thereby preventing deterioration in thermal insulation. The material employed for freezing containers are roughly classified into frame material, external-wall material, and internal-wall material. In most cases, the internal-wall material is formed of cold-rolled annealed steel without painting, and is preferably formed with low-temperature toughness, and accordingly, in many cases, SUS304, which is austenitic stainless steel, stipulated by JIS (Japanese Industrial Standard, which will be referred to as "JIS" hereafter) G 4305 as a steel member is employed. The aforementioned SUS304 exhibits excellent low-temperature toughness, high elongation performance, small yield ratio (yield stress/tensile strength), and a high work hardening coefficient, thereby serving as stainless steel with excellent impact toughness which has the advantage that the member formed thereof is not readily punctured in the event that the member suffers impact. However, SUS304 has the serious disadvantage of high costs. On the other hand, the steel used for the frame material and the external-wall material are assumed to be painted. The cold-rolled annealed steel is employed as the external-wall member, wherein while the SUS304, which is austenitic stainless steel, is employed for high-grade freezing containers, ferritic or martensitic stainless steel containing Cr of around 11% such as SUS410L or SUS410S stipulated by JIS G 4305 is also employed due to high costs of the aforementioned SUS304. The frame material is formed of hot rolled annealed sheets, and particularly, in many cases, are formed of 11%-Cr martensitic stainless steel with reduced C and N.

[0003] As the 11%-Cr-containing steel employed for container material, for example, martensitic stainless steel for welded structural materials is known as disclosed in Japanese Examined Patent Publication No. 51-13463, containing Cr of 10 to 18% by weight, Ni of 0.1 to 3.4%, Si of 1.0% by weight or less, and Mn of 4.0% by weight or less, and furthermore, reducing C to 0.03% by weight or less, and N to 0.02% by weight or less, so that massive martensitic structure is formed in a welded heat-affected zone, thereby improving ductility and toughness in the welded heat-affected zone. Furthermore, structural martensitic stainless steel is known as disclosed in Japanese Examined Patent Publication No. 57-28738, containing Cr of 10 to 13.5% by weight, Si of 0.5% by weight or less, and Mn of 1.0 to 3.5% by weight, reducing the concentration of C to 0.02% by weight or less, and the concentration of N to 0.02% by weight or less, and furthermore, suppressing Ni to less than 0.1% by weight, thereby exhibiting toughness and workability in a welded heat-affected zone without pre-heating and post-heating before and after welding. The aforementioned steel is employed for various structural materials such as frame members of offshore containers and the like, as disclosed in JOURNAL OF THE JAPAN WELDING SOCIETY, Vol. 57 (1988), No. 6, p. 432. Such 11%-Cr stainless steel is employed in frame members for container, or steel members for external-wall members, due to relatively low costs thereof. Accordingly, there is great demand for development of a technique for solving the problem of poor low-temperature and poor impact toughness as compared with the SUS304 which is austenitic stainless steel, and for enabling further reduction of costs thereof by reducing Cr-concentration, omission of annealing after hot rolling, and the like.

[0004] In order to solve the above-described problems, building-structural ferritic stainless steel is known as disclosed in Japanese Unexamined Patent Application Publication No. 11-302795, containing Cr of 8 to 16% by weight, Si of 0.05 to 1.5% by weight, and Mn of 0.05 to 1.5% by weight, and furthermore, suppressing C to 0.005 to 0.1%, N to 0.05% by weight or less, and (C + N) to 0.1% by weight or less, wherein the components thereof are adjusted such that martensitic structure is formed with a volume ratio of 50% or more in a welded heat-affected zone. However, the aforementioned steel disclosed in Japanese Unexamined Patent Application Publication No. 11-302795 does not exhibit sufficient low-temperature toughness required for freezing containers, and is to be used without any processing after hot rolling, or is to be used with heat treatment or pickling after hot rolling, and no consideration has been given to the poor corrosion resistance after painting.

[0005] Furthermore, a technique for forming hot-rolled steel without annealing is disclosed in Japanese Unexamined Patent Application Publication No. 11-302737, wherein steel containing Cr of 8 to 16% by weight, Si of 0.05 to 1.5%, Mn of 0.05 to 1.5%, and Ni of 0.05 to 1%, and furthermore, suppressing C to 0.005 to 0.1%, N to 0.05% or less, and (C + N) to 0.1% or less, is heated at 1100 to 1250°C, hot-rolling is completed under a temperature of 800°C or more,

coiling is made under a temperature of 700°C or less, and cooling is performed with a cooling rate of 5°C per minute or less, but with this technique, the steel is to be used without any processing after hot rolling, or is to be used with heat treatment or pickling after hot rolling, and no consideration has been given to the poor corrosion resistance after painting.

[0006] Furthermore, a technique for forming structural hot-rolled steel without annealing is disclosed in Japanese Patent Application No. 2003-141462 (corresponding to European Patent No. 03015110.4, Filing Date: July 3, 2003), which has been proposed by the present inventors, wherein steel containing Cr of 8 to 10% by mass, Si of 0.01 to 1.0% by mass, Mn of 0.01 to 0.30% by mass, Cu of 0.01 to 1.0% by mass, Ni of 0.01 to 1.0% by mass, and V of 0.01 to 0.20% by mass, is heated at 1100 to 1280°C, hot-rolling is completed under a temperature exceeding 930°C, coiling is made under a temperature exceeding 810°C, and cooling is performed with a cooling rate of 2°C per minute or less in the temperature range between 800 to 400°C. However, the aforementioned steel member disclosed in Japanese Patent Application No. 2003-141462 is to be used after pickling after hot rolling without painting, and furthermore, no method has been known for improving the surface properties by controlling pickling so as to improve corrosion resistance after painting, which is an essential component of the present invention.

[0007] In order to solve the above-described problems of the conventional techniques, it is an object of the present invention to provide structural Cr-containing steel, particularly to Cr-containing steel employed for freezing containers, with excellent low-temperature toughness and impact toughness, with low costs as compared with the austenitic stainless steel, and with sufficient corrosion resistance.

[0008] In most cases, various painting is made on the surface of the steel members used for freezing containers from the perspective of improvement of corrosion resistance, and in particular, from the perspective of appearance. Accordingly, the corrosion resistance after painting is an important performance, and it has been revealed from the research by the present inventors that it is necessary for the aforementioned steel material to exhibit corrosion resistance wherein a steel sample subjected to formation of cross-cuts after painting does not exhibit marked outflow rust after 1000-hour salt spray testing.

Disclosure of Invention

[0009] In order to solve the above-described problems, the present inventors intensely researched the influence of additive elements upon the above-described properties of the Cr-containing steel, and as a result, it has been revealed that the Cr-containing steel with Cr-concentration of 6.0 to 10.0%, and with C-concentration of 0.02% or less and N-concentration of 0.02% or less, exhibits both sufficient corrosion resistance, toughness, and impact toughness, required for structural Cr-containing steel, particularly required for steel used for freezing containers, manufacturing can be made with low costs as compared with austenitic stainless steel, and furthermore, annealing for hot-rolled steel can be omitted, thereby enabling manufacturing with lower costs. Furthermore, it has been revealed that the method serves as important means for improving corrosion resistance after painting, wherein the removal amount of the steel surface layer in descaling of hot-rolled steel is controlled so as to exhibit both the sufficient steel-surface properties and the sufficient corrosion resistance after descaling. The present invention has been made as follows based upon the above-described information.

[0010] That is to say, structural Cr-containing steel according to the present invention comprises: 0.002 to 0.02% by mass of C; 0.002 to 0.02% by mass of N; 0.05 to 1.0% by mass of Si; 0.05 to 1.0% by mass of Mn; 0.04% by mass or less of P; 0.02% by mass or less of S; 0.001 to 0.1% by mass of Al; 6.0 to 10.0% by mass of Cr, and the balance being Fe and unavoidable impurities, and the Cr-concentration in the surface layer of the steel is equal to or more than the value wherein 1% by mass is subtracted from the Cr-concentration within the steel.

[0011] Also, the present invention is structural Cr-containing steel which, in the above steel according to the invention, further comprises Cu of 0.1 to 1.0% by mass.

[0012] Also, the present invention is structural Cr-containing steel which, in the above steel according to the invention, further comprises at least one of: 0.1 to 1.0% by mass of Ni; and 0.1 to 1.0% by mass of Mo.

[0013] Also, the present invention is structural Cr-containing steel which, in the above steel according to the invention, further comprises at least one of: 0.005 to 0.10% by mass of Nb; and 0.005 to 0.20% by mass of V.

[0014] Also, the present invention is a manufacturing method for structural Cr-containing hot-rolled steel comprising: a step wherein a steel material comprising: 0.002 to 0.02% by mass of C; 0.002 to 0.02% by mass of N; 0.05 to 1.0% by mass of Si; 0.05 to 1.0% by mass of Mn; 0.04% by mass or less of P; 0.02% by mass or less of S; 0.001 to 0.1% by mass of Al; 6.0 to 10.0% by mass of Cr; and the balance being Fe and unavoidable impurities, is formed into a steel strip by hot rolling after reheating followed by a descaling process; wherein the steel surface is removed by a removal depth of 10 to 200 μm by descaling.

[0015] Also, the present invention is a manufacturing method for structural Cr-containing cold-rolled steel, wherein following the descaling processing in the manufacturing method of the above steel according to the invention, cold rolling, annealing cold-rolled steel, and pickling are performed.

[0016] Also, the present invention is a manufacturing method for structural Cr-containing steel which, in the manufacturing method for the above steel according to the invention, further comprises Cu of 0.1 to 1.0% by mass.

[0017] Also, the present invention is a manufacturing method for structural Cr-containing steel which, in the manufacturing method for the above steel according to the invention, further comprises at least one of: 0.1 to 1.0% by mass of Ni; and 0.1 to 1.0% by mass of Mo.

[0018] Also, the present invention is a manufacturing method for structural Cr-containing steel which, in the manufacturing method for the above steel according to the invention, further comprises at least one of: Nb of 0.005 to 0.10% by mass; and V of 0.005 to 0.20% by mass.

[0019] Also, the present invention is structural Cr-containing steel wherein the above steel according to the invention is employed for freezing containers.

[0020] Also, the present invention is a manufacturing method for structural Cr-containing hot-rolled steel wherein, in the manufacturing method for the above steel according to the invention, the structural Cr-containing steel is employed for frame members of freezing containers.

[0021] Also, the present invention is a manufacturing method for structural Cr-containing cold-rolled steel wherein, in the manufacturing method for the above steel according to the invention, the structural Cr-containing steel is employed for external-wall members of freezing containers.

[0022] Also, the present invention is a freezing container which is formed of the above-described Cr-containing steel, wherein formation of the freezing container is made by forming and welding, and the steel surface is coated with dry-paint film thickness of 10 μm or more.

[0023] Also, the present invention is Cr-containing steel wherein the above-described structural steel according to the invention is used for civil engineering and construction.

[0024] Also, the present invention is a manufacturing method for structural Cr-containing hot-rolled steel, wherein the above-described steel according to the invention is used for civil engineering and construction.

[0025] Also, the present invention is a manufacturing method for structural Cr-containing cold-rolled steel, wherein the above-described steel according to the invention is used for civil engineering and construction.

Brief Description of the Drawings

[0026]

Fig. 1 is a diagram which shows the relation between the removal depth of the steel surface layer and rust area ratio after SST (Salt Spray Testing).

Fig. 2A is a scanning electron micrograph which shows the surface of the steel subjected to surface removal with the removal depth of 8 μm .

Fig. 2B is a scanning electron micrograph which shows the surface of the steel subjected to surface removal with the removal depth of 40 μm .

Fig. 3A is a chart which shows concentration profiles of Fe and Cr for the steel subjected to surface removal with the removal depth of 8 μm , in the thickness direction from the surface of the steel by glow discharge optical emission spectroscopy.

Fig. 3B is a chart which shows concentration profiles of Fe and Cr for the steel subjected to surface removal with the removal amount of 40 μm , in the thickness direction from the surface of the steel by glow discharge optical emission spectroscopy.

Fig. 4 is a schematic diagram which shows a scale/steel interface.

Best Mode for Carrying Out the Invention

[0027] Description will be made regarding arrangements according to the present invention.

[0028] First, description will be made regarding the reasons that the components of the alloy according to the present invention are restricted to the above-described range. Note that "% by mass" will be used as the unit of the concentration of the components, which will be abbreviated to "%" hereafter.

(1) C: 0.002 to 0.02%

[0029] The lower the concentration of C is, the corrosion resistance after painting is more preferably improved. The reason is that generation of a Cr depleted layer due to precipitation of carbonitride is suppressed. However, while an arrangement with the concentration of C less than 0.002% exhibits shortage of strength, an arrangement with the concentration of C exceeding 0.02% exhibits shortage of toughness and ductility, leading to deterioration in impact toughness. With the steel according to the present invention, it is important that the steel is formed with reduced con-

centration of C of 0.02% or less. Furthermore, with the present embodiment, the steel is formed with the concentration of C of 0.02% or less, thereby enabling omission of annealing for hot-rolled steel. Accordingly, with the present embodiment, the steel is formed with the concentration of C in a range of 0.002 to 0.02%. The steel is preferably formed with the concentration of C in a range of 0.003 to 0.013%, is more preferably formed with the concentration of C in a range of 0.003 to 0.008%, and further preferably formed with the concentration of C in a range of 0.003 to 0.005%, from the perspective of improvement of corrosion resistance after painting.

(2) N: 0.002 to 0.02%

[0030] The lower the concentration of N is, the corrosion resistance after painting is more preferably improved, in the same way as with C. However, while an arrangement with the concentration of N less than 0.002% exhibits shortage of strength, an arrangement with the concentration of N exceeding 0.02% exhibits shortage of toughness and ductility, leading to deterioration in impact toughness. With the steel according to the present invention, it is important that the steel is formed with reduced concentration of N of 0.02% or less. Furthermore, with the present embodiment, the steel is formed with the concentration of N of 0.02% or less, thereby enabling omission of annealing for hot-rolled steel. Accordingly, with the present embodiment, the steel is formed with the concentration of N in a range of 0.002 to 0.02%. The steel is preferably formed with the concentration of N in a range of 0.0030 to 0.0060% from the perspective of improvement of corrosion resistance after painting.

(3) Si: 0.05 to 1.0%

[0031] While Si is an element which is effectively used as a deoxidizing agent, the steel formed with the concentration of Si less than 0.05% does not exhibit sufficient deoxidation, and accordingly, the steel needs to be formed with the concentration of Si of 0.05% or more. However, the steel with the concentration of Si exceeding 1.0% exhibits shortage of toughness and ductility, leading to deterioration in impact toughness. Accordingly, with the present embodiment, the steel is formed with the concentration of Si in a range of 0.05 to 1.0%. The steel is preferably formed with the concentration of Si in a range of 0.1 to 0.5% from the perspective of improvement of low-temperature toughness.

(4) Mn: 0.05 to 1.0%

[0032] While Mn is an element which is effectively used as a deoxidizing agent in the same way as with Si, the steel formed with the concentration of Mn less than 0.05% does not exhibit sufficient deoxidation, and accordingly, the steel needs to be formed with the concentration of Mn of 0.05% or more. However, the steel with the concentration of Mn exceeding 1.0% exhibits deterioration in corrosion resistance due to increased MnS-inclusion. Accordingly, with the present embodiment, the steel is formed with the concentration of Mn in a range of 0.05 to 1.0%. The steel is preferably formed with the concentration of Mn in a range of 0.10 to 0.30% from the perspective of improvement of corrosion resistance after painting.

(5) P: 0.04% or less

[0033] P is an element which causes adverse effects upon corrosion resistance, as well as upon mechanical properties such as toughness, ductility, and the like, and particularly, the steel with concentration of P exceeding 0.04% exhibits marked adverse effects thereupon, and accordingly, the steel according to the present embodiment is formed with restricted concentration of P of 0.04% or less. In particular, the steel required to exhibit high corrosion resistance after painting is preferably formed with the concentration of P of 0.02% or less.

(6) S: 0.02% or less

[0034] S is combined with Mn to form MnS, leading to initial rust-formation portions. Furthermore, S is an adverse-effect element which causes intergranular segregation thereof, leading to brittleness, and accordingly, the steel is preferably formed with the concentration of S as low as possible. In particular, the steel with the concentration of S exceeding 0.02% exhibits marked adverse effects, and accordingly, the steel is formed with restricted concentration of S of 0.02% or less. In particular, the steel required to exhibit high corrosion resistance after painting is preferably formed with the concentration of S of 0.006% or less.

(7) Al: 0.001 to 0.1%

[0035] While Al is an element which is effectively used as a deoxidizing agent, and furthermore has the advantage

of improving ductility by spheroidizing oxide, the steel formed with the concentration of Al less than 0.001% does not exhibit the aforementioned sufficient advantage, and accordingly, the steel needs to be formed with the concentration of Al of 0.001% or more. However, the steel with the concentration of Al exceeding 0.1% exhibits deterioration in corrosion resistance due to increased inclusions. Accordingly, the steel is formed with the concentration of Al in a range of 0.001 to 0.1%. Note that the steel containing excessive Al may cause formation of inclusions, leading to deterioration in mechanical properties, and accordingly, the steel is preferably formed with the maximal concentration of 0.05% from the perspective of workability of hot-rolled steel.

(8) Cr: 6.0 to 10.0%

[0036] Cr is a necessary element for maintaining corrosion resistance required for materials for freezing containers, which is the object of the present invention. The external-wall members for the freezing containers are used with painting, and accordingly, is not required to exhibit high corrosion resistance as compared with SUS304, but the steel with the concentration of Cr less than 6.0% does not exhibit sufficient corrosion resistance. However, the steel with the concentration of Cr exceeding 10.0% exhibits shortage of toughness and ductility, leading to deterioration in impact toughness. As an important fact according to the present invention, it has been revealed that steel with the concentration of Cr in a range of 6.0% to 10.0% exhibits sufficient corrosion resistance, as well as sufficient toughness and impact toughness, required for materials for freezing containers. Furthermore, with the present embodiment, the steel is formed with the concentration of Cr of 10.0% or less, thereby enabling omission of annealing for hot-rolled steel. Note that in order to form hot-rolled steel without annealing with sufficient low-temperature toughness, the steel is preferably formed with a concentration of Cr in a range of 6.0 to 9.5%. Furthermore, the steel is more preferably formed with a concentration of Cr in a range of 6.0 to 9.0%.

[0037] While description has been made regarding basic components, an arrangement may be made wherein the steel is formed with other components for further improving corrosion resistance as follows.

(9) Cu: 0.1 to 1.0%

[0038] Cu is an element which is effectively used for reducing corrosion rate, thereby improving corrosion resistance, and furthermore, has the advantage of suppressing crevice corrosion. With the corrosion resistance after painting which is the object of the present invention, corrosion in the crevice structure partially subjected to exfoliation of painting is a serious problem, and accordingly, the steel needing to exhibit high corrosion resistance after painting is preferably formed with addition of Cu. However, the steel with the concentration of Cu less than 0.1% does not exhibit the aforementioned sufficient advantages, and on the other hand, the steel with the concentration of Cu exceeding 1.0% readily causes deterioration in ductility and impact toughness, and furthermore, readily causes hot cracking during hot rolling. Accordingly, the steel is preferably formed with the concentration of Cu in a range of 0.1 to 1.0%. Note that the steel is preferably formed with the maximal concentration of Cu of 0.7% from the perspective of prevention of hot cracking, and workability.

(10) Ni: 0.1 to 1.0%

[0039] Ni is an element which is effectively used for reducing corrosion rate, thereby improving corrosion resistance, as well. Furthermore, Ni is a component which is effectively used for improving toughness. However, the steel with the concentration of Ni less than 0.1% does not exhibit the aforementioned sufficient advantages, and on the other hand, Ni is an extremely high-cost material, and accordingly, the steel formed with the concentration of Ni exceeding 1.0% leads to high costs, and accordingly, the steel is preferably formed with the concentration of Ni in a range of 0.1% to 1.0%. Note that the steel is preferably formed with the maximal concentration of Ni of 0.5% from the perspective of prevention of excessive hardness and high costs.

(11) Mo: 1.0% or less

[0040] Mo is an element which is effectively used for reducing corrosion rate, thereby improving corrosion resistance. However, the steel with the concentration of Mo less than 0.1% does not exhibit the aforementioned sufficient advantages, and on the other hand, Mo is an extremely high-cost material as with Ni, and accordingly, the steel formed with the concentration of Mo exceeding 1.0% leads to high costs, and furthermore exhibits deterioration in ductility, and accordingly, the steel is preferably formed with the concentration of Mo in a range of 0.1% to 1.0%. Note that the steel is preferably formed with the concentration of Mo in a range of 0.1% to 0.5% from the perspective of balance between the corrosion resistance, and the strength and workability.

(12) Nb: 0.005 to 0.10%

[0041] Addition of Nb leads to precipitation of Nb-carbonitride during hot rolling, thereby suppressing growth of grains, and thereby drastically reducing the size of the grains in the steel after hot rolling. In particular, the steel required to exhibit high low-temperature toughness is preferably formed with addition of Nb. However, the steel with the concentration of Nb less than 0.005% does not exhibit the aforementioned sufficient advantage, and on the other hand, the steel formed with the concentration of Nb exceeding 0.10% exhibits deterioration in toughness at a welded portion, and accordingly, addition of Nb is determined to be 0.005 to 0.10%. The steel is preferably formed with the maximal concentration of Nb of 0.06% from the perspective of toughness at a welded portion.

(13) V: 0.005 to 0.20%

[0042] Addition of V leads to precipitation of V-carbonitride or V_4C_3 during hot rolling, and has the advantage of reducing the size of the grains in the steel after hot rolling, thereby exhibiting the advantage of improving low-temperature toughness of steel as with Nb, but the steel with the concentration of V less than 0.005% does not exhibit the aforementioned sufficient advantages, and on the other hand, the steel with the concentration of V exceeding 0.20% leads to the adverse effects of deterioration in toughness of a welded portion and base material.

Accordingly, the steel is formed with the concentration of V in a range of 0.005% to 0.20%. Note that the steel is formed with the maximal concentration of V of 0.15% from the perspective of improvement of toughness of the base material.

[0043] The components other than the aforementioned ones include Fe and unavoidable impurities.

(14) Microstructures in steel

[0044] Next, description will be made regarding microstructures in the steel. The steel manufactured with the technique according to the present invention is substantially formed with a ferritic single phase microstructure. While the steel subjected to cooling after hot rolling may partially contain bainite, the steel subjected to cold rolling and annealing substantially exhibits a ferritic single phase microstructure. With the steel according to the present invention, the components thereof are designed such that the steel prior to processing, such as the steel after hot rolling, the steel after cold rolling and annealing, or the like, does not exhibit formation of a hard martensitic microstructure. On the other hand, the components thereof are designed such that the welded portions thereof are formed with a low-carbon, low-nitrogen containing martensitic microstructure, thereby exhibiting an excellent property of sufficient low-temperature toughness even after assembly with welding.

(15) Manufacturing method of the steel

[0045] Next, description will be made regarding a manufacturing method for the steel according to the present invention. First, smelting processing is performed with a smelting furnace such as a converter, an electric heating furnace, or the like, following which the molten steel is subjected to refining so as to adjust the components thereof to those according to the present invention with the VOD method, the AOD method, the RH method, or the like, and subsequently, the molten steel is formed into slabs with the continuous casting method, or the casting slabbing method. Subsequently, the slab is heated, and subjected to hot-rolling processing so as to form a hot-rolled steel. Furthermore, an arrangement may be made wherein the slab after casting is inserted into a heating furnace prior to cooling to the room temperature, or an arrangement may be made wherein the slab after casting is directly subjected to hot rolling. While the slab-reheating temperature for hot rolling at the time of reheating the slab is not restricted to the particular one, the coiling temperature needs to be set to a high temperature in order to omit the annealing processing for the hot-rolled steel, and accordingly, the slab-reheating temperature is preferably set to 1050°C or more. On the other hand, processing performed under the reheating temperature exceeding 1250°C leads to a problem of sagging of the slab, as well as a problem of loss due to oxidization of the surface of the slab. Furthermore, in some cases, this leads to a problem of deterioration in workability in hot rolling due to partial formation of δ -ferritic phase microstructure, depending upon the components of the steel. While the reduction and temperature conditions during roughing hot rolling are not restricted to particular ones, at least one or more passes of rolling with rolling reduction of 30% or more is preferably performed. This high-reduction rolling leads to reduction of the size of grains in the steel, thereby improving the low-temperature toughness of the base material. The finishing temperature in hot rolling is set to 900°C or more, and is preferably set to a temperature exceeding 930°C, from the perspective of enhancement of softening after coiling. With the present embodiment, the finishing temperature in hot rolling set to 900°C or more prevents formation of deformed ferrite grains due to rolling in the $\alpha+\gamma$ two phase region, and furthermore, maintains the high coiling temperature, thereby preventing formation of a hard martensitic phase microstructure during cooling after coiling. The coiling temperature in hot rolling is set to 800°C or more, and is preferably set to 810°C or more, from the perspective

of softening after coiling. Furthermore, an arrangement may be made wherein annealing is performed for hot-rolled steel as necessary in the event that the steel needs to be subjected to adjustment of strength after hot rolling, or the like. Batch annealing or continuous annealing may be performed under temperature of 600°C or more for the aforementioned annealing of the hot-rolled steel. With the aforementioned batch annealing, the annealing is preferably for one hour or more. Subsequently, a scale layer and the surface of the steel is removed by shot blasting, pickling, or the like. An arrangement may be made wherein the steel after hot rolling, after hot rolling and hot annealing, or after descaling, is subjected to rolling process by skin pass rolling from the perspective of adjustment of the shape.

(16) Removal amount of the steel surface in descaling processing

[0046] The removal amount of descaling processing is an important factor having the great influence upon the corrosion resistance after painting which is the object of the present invention. Here, as shown in a schematic diagram in Fig. 4, "removal depth of the steel surface 1" denotes the thickness in the depth direction from a so-called scale/steel interface 2 including an internal oxide layer 3 and a Cr depleted layer 4. A scale layer 5 is generally formed of iron oxide and chromium oxide on the surface of the steel after hot rolling, or after hot rolling and annealing, wherein a spinel structure phase generally formed of Fe serves as the outer layer thereof, and a spinel structure phase generally formed of Fe and Cr serves as the inner layer thereof. It is known that in the event that the steel is exposed to high temperature for a long time after hot rolling and coiling or the like, Cr is dominantly oxidized due to growth of the scale layer 5 near the steel, leading to shortage of supply due to diffusion of Cr from the inside of the steel, and leading to formation of Cr depleted layer 4 immediately underneath the scale layer.

The remaining Cr depleted layer 4 on the surface of the steel after descaling causes marked deterioration in corrosion resistance, and accordingly, it is important for the descaling processing to completely remove the Cr depleted layer 4 on the surface of the steel. With the steel containing Cr of 11% or more, i.e., the stainless steel, a fine-structured layer generally formed of Cr_2O_3 serves as a continuous further-inner layer as to the aforementioned spinel layer, leading to suppression of diffusion of oxygen from the outside toward the inside of the steel. Accordingly, the Cr depleted layer 4 is formed with the thickness from the scale/steel interface being less than 10 μm at most. However, with the steel with the low Cr concentration of 10% or less as with the present invention, the Cr_2O_3 layer is not continuously formed, leading to marked diffusion of oxygen from the outside, and leading to formation of the so-called internal oxidized layer 3 as shown in Fig. 4. The internal oxide layer 3 is formed due to elements with high oxygen affinity such as Cr, Si, or the like, being dominantly oxidized, which can be confirmed by observing dominant oxidation 6 in the grain-boundary of the steel or oxide formation 7 inside the grains on the cross-sectional sample of the steel. According to the present invention, the processing is an important factor, wherein both the internal oxide layer 3 formed on the inner side of the scale/steel interface 2, and the Cr depleted layer 4 formed due to formation of the aforementioned internal oxide layer 3, are removed by descaling processing, thereby drastically improving corrosion resistance after painting.

[0047] Furthermore, the present inventors have performed intense study from the perspective of painting adhesion. As a result, it has been revealed that the steel subjected to descaling by pickling after hot rolling may suffer marked grain boundary erosion, leading to deterioration in painting adhesion to the steel since sufficient paint cannot flow into the eroded grain boundary portion due to poor wettability of the high-viscosity paint. In particular, the amount of Cr in the grain boundary is readily reduced in the portion containing the Cr depleted layer as described above, readily leading to grain boundary erosion in this portion. Reduction of painting adhesion readily causes formation of the crevice structure between the paint film and the steel, leading to deterioration in corrosion resistance after painting.

[0048] The conditions for obtaining both the sufficient painting adhesion and the corrosion resistance after painting have been studied based upon the above-described information. Fig. 1 and Table 1 show an example of evaluated results of the corrosion resistance of the steel and corrosion resistance after painting over the removal amount of the steel surface, wherein 9%-Cr-containing hot-rolled steel manufactured in a plant is employed as a sample, and is subjected to descaling by shot blasting and pickling with sulfuric acid and hydrofluoric acid / nitric acid in a laboratory. As can be understood from these results, with the steel containing Cr of 6.0 to 10.0%, removal of the steel surface of 10 μm or more in the descaling step improves painting adhesion and corrosion resistance after painting, as well as improving corrosion resistance of the steel. Furthermore, making the difference in Cr concentration, i.e., (Cr-concentration within the steel) - (Cr-concentration in the surface layer of the steel), to be within 1%, improves corrosion resistance after painting by reducing the roughness due to the grain boundary erosion described below, as well as improving corrosion resistance on the surface of the steel. That is to say, the steel subjected to removal processing with the removal depth of 10 μm or more exhibits the difference in Cr concentration, i.e., (Cr-concentration within the steel) - (Cr-concentration in the surface layer of the steel), of 1% or less, and in this case, exhibits excellent corrosion resistance after painting. Here, the Cr-concentration within the steel means the Cr-concentration near the middle portion in the thickness direction of the steel, which is not affected by the Cr depleted layer, or the Cr-concentration of the inside portion at the depth exceeding 200 μm from the surface thereof in a case of hot-rolled steel or hot-rolled annealed steel. In a case of cold-rolled annealed steel, the Cr-concentration within the steel means the Cr-concentration at the

portion at the depth of $t/4$ or more, wherein t denotes the thickness of the steel. The Cr-concentration can be measured with a method such as EPMA, EDX, the analysis method using fluorescent X-ray or the like, the solid emission spectroscopic analysis method, the method wherein chemical solution of the steel is subjected to quantitative analysis with the Inductively Coupled Plasma-Atomic Emission (which will be referred to as "ICP method" hereafter) or the titrimetric analysis, or the like. In a case of employing EPMA analysis or the like, which obtains measurement results of Cr-concentration at a particular portion, there is the need to select the portion which is to be measured so as not to be affected by segregation formed at middle portion in the thickness direction of the steel.

[0049] Fig. 2 shows results obtained by observing the surface of the steel subjected to the surface removal with the removal depth of the steel surface of $8\text{ }\mu\text{m}$ and $40\text{ }\mu\text{m}$ using a scanning electron microscope. With the example subjected to surface removal with the removal amount of the steel surface of $8\text{ }\mu\text{m}$, the grain boundary where dominant and marked erosion has occurred was observed. On the other hand, with the example subjected to surface removal with the removal amount of the steel surface of $40\text{ }\mu\text{m}$, the grain boundary where marked erosion has occurred was not observed.

[0050] Fig. 3 shows measurement results of the concentration profiles of Fe and Cr in the thickness direction from the surface of the steel by glow discharge optical emission spectroscopy (GDS). While with the steel subjected to surface removal with the removal depth of the steel surface of $8\text{ }\mu\text{m}$, the remaining Cr depleted layer was observed near the surface of the steel, with the steel subjected to surface removal with the removal depth of the steel surface of $40\text{ }\mu\text{m}$, the remaining Cr depleted layer was not observed. These steel samples were subjected to measurement of Cr-concentration using the Electron Probe Micro Analyzer (EPMA), wherein the measurement results were obtained that while $8\text{-}\mu\text{m}$ -layer-removed steel exhibits reduction of Cr-concentration by 2.5% by mass as compared with the Cr-concentration within the steel (the concentration evaluated with the ICP method for the steel sample subjected to surface removal with the removal amount of the steel surface of $500\text{ }\mu\text{m}$: 9% by mass), $40\text{-}\mu\text{m}$ -layer-removed steel exhibits the Cr-concentration generally equal to the Cr-concentration within the steel. Furthermore, as the result of measurement of the whiteness of the surface of the steel stipulated by JIS Z 8715, while $8\text{-}\mu\text{m}$ -layer-removed steel exhibits the whiteness index of approximately 62, $40\text{-}\mu\text{m}$ -layer-removed steel exhibits the whiteness index of 68. As a result of research of the whiteness of various kinds of hot-rolled steel, in general, the hot-rolled steel with the whiteness index of 65 or more does not contain marked erosion of the grain boundary, thereby improving the corrosion resistance of the steel after painting. Note that the whiteness was measured using a spectrophotometer, wherein the CM-1000 manufactured by Minolta Corporation was employed.

[0051] As described above, it is assumed that in the event that the removal depth of the steel surface does not reach $10\text{ }\mu\text{m}$, the internal oxide layer 3 and the Cr depleted layer 4 are not completely removed, leading to deterioration in painting adhesion due to erosion of the grain boundary, and leading to deterioration in corrosion resistance after painting, as well as leading to insufficient corrosion resistance of the steel. Note that surface removal with the removal depth of the steel surface exceeding $200\text{ }\mu\text{m}$ may lead to problems of deterioration in corrosion resistance and deterioration in the appearance of the steel, due to formation of so-called smut adhered to the surface of the steel during pickling, as well as leading to increased costs due to excessive loss by descaling. The removal depth of the steel surface is more preferably determined to $15\text{ }\mu\text{m}$ or more, and is further preferably determined to $20\text{ }\mu\text{m}$ or more.

[0052] Control of the surface properties by removing the steel surface of Cr-containing steel, and improvement of corrosion resistance after painting by removing the internal oxide layer 3 and the Cr depleted layer 4, based upon the detailed information obtained through intense study are the important factors of the present invention, and as a result of the information through intense study, it has been revealed that the steel is preferably subjected to surface removal with the removal depth of $10\text{ }\mu\text{m}$ or more, is more preferably subjected to surface removal with the removal depth of $15\text{ }\mu\text{m}$ or more, and is further preferably subjected to surface removal with the removal depth of $20\text{ }\mu\text{m}$ or more, while maintaining the Cr-concentration in the surface layer of the steel of the value of (Cr-concentration within the steel - 1% by mass) or more, thereby markedly improving corrosion resistance after painting.

[0053] Note that the corrosion resistance of the steel shown in Table 1 was evaluated with the rust area ratio after 4-hours salt spray test stipulated by JIS Z 2371, wherein a sample exhibiting a rust area ratio of 20% or less is determined as a sample exhibiting excellent corrosion resistance. On the other hand, the corrosion resistance after painting was evaluated with the method wherein a steel sample is coated with acrylic resin paint with an intended dry film thickness of $50\text{ }\mu\text{m}$, is subjected to formation of cross-cuts on the surface thereof, following which the steel sample is subjected to 1000-hour salt spray testing stipulated by JIS Z 2371, and the steel sample wherein marked outflow rust such as formation of a rust pool at the lower portion of the sample, is not observed, is determined as a steel sample with excellent corrosion resistance after painting. On the other hand, the specific measurement method for obtaining the removal depth of the steel surface is that the weight and size of the sample following mechanical removal of the scale by shot blasting, and the weight thereof after pickling, are measured, the difference in weight therebetween is divided by the surface area of the sample so as to calculate the removal amount of the steel (g/cm^2), following which the removal thickness (depth) (μm) of the steel is calculated using the density of the steel ($7.8\text{g}/\text{cm}^3$).

[0054] Note that the descaling method for hot-rolled steel employed in the present invention is not restricted to a

particular one. Various known methods which may be employed in the present invention include mechanical removal methods by shot blasting, brushing, or using a small-diameter roller, chemical removal methods using hydrochloric acid, sulfuric acid, nitric acid, hydrofluoric acid, hydrofluoric/nitric acid, ferric chloride solution, and the like.

(17) Processing after descaling

[0055] The steel after descaling described above may be employed as the steel according to the present invention. Furthermore, an arrangement may be employed as the steel according to the present invention, wherein the steel after the aforementioned descaling is subjected to cold rolling so as to be formed with a predetermined thickness, following which the cold-rolled steel is subjected to annealing and pickling. The surface of the cold-rolled annealed steel is sufficiently smooth, and accordingly, it is assumed that deterioration in corrosion resistance does not occur due to poor painting adhesion described above, but in the event that insufficient descaling has been performed after hot rolling, the steel does not exhibit sufficient corrosion resistance after cold rolling, as well. With the steel according to the present invention, the internal oxide layer 3 and the Cr depleted layer 4 immediately underneath the scale are completely removed by descaling for hot-rolled steel, thereby exhibiting sufficient corrosion resistance even after cold rolling and annealing. Cold rolling is preferably performed with rolling reduction of 30% or more. The steel after cold rolling is preferably subjected to annealing in order to soften the steel under annealing temperature of 600°C or more. The steel after cold rolling and annealing is subjected to pickling or similar processing, following which various finishing processing may be performed stipulated by JIS Z 4305. Giving consideration to the corrosion resistance after painting, No. 2B finishing is preferably employed.

(18) Painting method

[0056] Painting is made by spray painting, brush painting, or the like, using various kinds of paints stipulated by JIS K 5500, such as an acrylic resin paint, phthalic resin paint, epoxy resin paint, polyurethane resin paint, or the like. Furthermore, the steel may be coated with various kinds of primers prior to painting for preventing initial rusting. Furthermore, the steel is subjected to under-coating or middle coating using various kinds of rust resisting paints or resin paints, as necessary. Note that the steel according to the present invention exhibits excellent adhesion between the surface thereof and a top coating paint, as well as exhibiting the high corrosion resistance of the steel itself as compared with common steel, thereby enabling omission of primer coating, under-coating, and middle coating, and thereby enabling directly coating of the steel with high-viscosity top-coating paint. Giving consideration to use for freezing containers, there is the need to coat the steel with the paint-film thickness of 10 μm or more for obtaining sufficient corrosion resistance. Note that with the steel according to the present invention, painting can be omitted, depending upon the use thereof, e.g., use for residential structural materials, and particularly for members which are not required to exhibit high corrosion resistance.

(19) Target for the mechanical properties of the steel according to the present invention

[0057] Giving consideration to use for structural steel, the steel is required to exhibit a Charpy impact value of 50 J/cm² or more at -25°C serving as an index value of the toughness. In particular, giving consideration to use for materials for freezing containers, or use for housing materials in the cold region, the steel is preferably formed with a Charpy impact value of 80 J/cm² or more at -25°C. While the steel is preferably formed so as to exhibit as great an elongation value as possible in the tensile test, the steel is required to exhibit the aforementioned elongation value of 30% or more to be formed in various kinds of shapes. Furthermore, while the steel is preferably formed so as to exhibit yield ratio as low as possible, wherein the yield ratio serves as an index value representing the degree of difficulty in workability and earthquake performance in a case of being employed as a housing material, the steel is required to exhibit the aforementioned yield ratio of 80% or less, and is preferably formed with the yield ratio of 75% or less, in a case of being employed as a structural material.

(20) Target for the corrosion resistance after painting of the steel according to the present invention

[0058] In most cases, the steel for freezing containers is subjected to various kinds of painting of the surface thereof from the perspective of improvement of corrosion resistance, and particularly from the perspective of appearance. Accordingly, the corrosion resistance after painting is an important factor.

[0059] The present inventors performed a detailed comparative study with regard to results of the corrosion resistance after painting of the steel which has been used in actuality, and the results obtained from the accelerated test by salt spraying, and as a result, it has been revealed that in the event that the sample of the steel subjected to painting, formation of cross-cuts, and 1000-hour salt spray testing, in that order, does not exhibit marked outflow rust, the steel

exhibits sufficient corrosion resistance in practical use thereof. Accordingly, corrosion resistance after painting was evaluated based upon the results obtained from the 1000-hour salt spray testing.

Examples

[0060] The steel materials were subjected to casting with the chemical composition shown in Table 2 so as to form a steel ingot of 50 kg by vacuum melting, heated up to 1200°C, and held under this temperature for one hour, following which the steel was subjected to hot rolling into hot-rolled steel with the thickness of 4 mm. The half of the samples of the hot-rolled steel were subjected to homogenizing annealing (hot-rolling annealing) under 650°C for ten hours. The hot-rolled steel without the subsequent processing and the hot-rolled annealed steel were subjected to descaling by shot blasting and subsequent pickling using mixed acid such as mixture of hydrofluoric acid and nitric acid so as to remove the steel surface by approximately 15 µm. Note that the measurement method for obtaining the removal amount of the steel surface is that the weight and size of the sample following mechanical removal of the scale by shot blasting, and the weight thereof after pickling, are measured, the difference in weight therebetween is divided by the surface area of the sample so as to calculate the removal amount of the steel (g/cm²), following which the removal thickness (depth) (µm) of the steel is calculated using the density of the steel (7.8g/cm³). Note that the steel was subjected to pickling using mixed acid formed of hydrofluoric acid solution of 1 to 2% by mass and nitric acid solution of 13 to 15% by mass under temperature of 40 to 60°C, and was repeatedly picked up for measuring the weight thereof following pickling every 30 seconds, thereby obtaining desired removal depth of the steel surface.

[0061] With the steel denoted by No. 1, the samples with various kinds of the removal depth of the steel surface were prepared as comparative examples. The Cr-concentration in the surface layer of the steel was obtained for these samples by making EPMA analysis. The aforementioned EPMA was performed with an accelerating voltage of 15 kV. It is assumed that the information obtained under the aforementioned conditions is generally reflected in the concentration in the depth range between the surface thereof and a depth of 0.5 µm. With the steel denoted by No. 1, the steel was subjected to surface removal with the removal depth of the steel surface of 500 µm, following which the steel sample was subjected to quantitative analysis using the ICP method, whereby the concentration was determined to be 9.1% by mass. While the steel samples subjected to surface removal with the removal depth of the steel surface of 5 µm and 8 µm exhibited Cr-concentrations of 5.1% by mass and 6.6% by mass, respectively, the steel sample subjected to surface removal with the removal depth of the steel surface of 15 µm exhibited 8.3% by mass, which was equal to or more than the (Cr-concentration within the steel - 1)%. Table 3 shows the results of Cr-concentration measurement for other steel samples under the same conditions. In any case, the steel sample subjected to surface removal with the removal depth of the steel surface of 15 µm exhibited Cr-concentration equal to or more than the (Cr-concentration within the steel - 1)%.

[0062] Plate samples of the size of (the thickness X 50 X 100 (mm)) were cut off from these hot-rolled steel products, were coated with acrylic-silicone resin paint (top coat with SILICOTECT AC manufactured by Kansai Paint Co., Ltd.) with intended dry paint thickness of 50 µm on the surface by spray painting, X-shaped cross-cuts were formed on the top layer including the aforementioned paint film, the prepared samples were subjected to the 1000-hour salt spray testing stipulated by JIS Z 2371 (5%-NaCl solution, 35°C, and pH 6.5 to 7.2), and the time was measured wherein marked outflow rust was generated, e.g., a rust pool was generated at the lower portion of the sample. Note that the dry film thickness of the paint film was measured by using an electromagnetic film thickness monitor and by observing the cross-section with microscope. The measured dry film thickness was approximately 50 µm. Furthermore, both surfaces of the steel sheet was ground by 0.75 mm so as to obtain the thickness of 2.5 mm, then Charpy-impact test samples of a sub-size wherein a V-shaped notch was formed with a depth of 2 mm perpendicular to the rolling direction, were obtained stipulated by JIS Z 2202, and the Charpy-impact value (J/cm²) was measured under -25°C stipulated by JIS Z 2242. The results are shown in Table 3. While the Charpy-impact value cannot be measured for a cold-rolled steel sheet with a thickness of 2 mm or less using a normal method, in general, the smaller the thickness of the steel is, the greater the toughness thereof is (for example, see JOURNAL OF THE JAPAN WELDING SOCIETY, Vol. 61, No. 8 (1992), p. 636), and since the cold-rolled steel has the advantage for Charpy-impact value as compared with the hot-rolled steel from the point of the microstructure, the cold-rolled steel exhibits Charpy-impact value under -25°C equal to or greater than that of the hot-rolled steel. Accordingly, in the event that the hot-rolled steel with a great thickness exhibits sufficient Charpy-impact value, the cold-rolled steel with small thickness formed of the same material as with the aforementioned hot-rolled steel exhibits a sufficient Charpy-impact value, as well. A cold-rolled annealed sample with a thickness of 0.7 mm was actually formed using the steel denoted by No. 2 without being subjected to annealing after hot-rolling, wherein a V-shaped notch was formed with a depth of 2 mm while maintaining the thickness of 0.7 mm, and the Charpy absorbed energy was measured for the prepared sample under -25°C, using a small-sized Charpy tester (100kgf = 98N), and as a result, the excellent result of 150 J/cm² was obtained.

[0063] Furthermore, the aforementioned hot-rolled steel subjected to pickling was subjected to cold rolling so as to be formed with thickness of 0.7 mm, following which the steel was subjected to annealing under 750°C for one minute,

and subsequently, the steel was subjected to descaling by electro-pickling in a neutral salt solution and nitric acid, whereby cold-rolled steel products were obtained. The aforementioned electro-pickling in a neutral salt solution was performed in a 20%-Na₂SO₄ solution under temperature of 70 to 80°C with the charge amount of 100 to 200 C/dm². On the other hand, the aforementioned electro-pickling in a nitric acid was performed in a 10%-HNO₃ solution under temperature of 50 to 60°C with the charge amount of 20 to 40 C/dm².

[0064] Tensile test samples were cut off from these cold-rolled steel products in the rolling direction stipulated by JIS13B, and tensile test was performed for these samples stipulated by JIS Z 2241, whereby the elongation and the yield ratio thereof were measured. Furthermore, plate samples of the size of (the thickness x 50 x 100 (mm)) were cut off from these cold-rolled steel products, were coated with acrylic-silicone resin paint (top coat with SILICOTECT AC manufactured by Kansai Paint Co., Ltd.) with intended dry paint thickness of 50 μm by surface spray painting, X-shaped cross-cuts were formed on the top layer including the aforementioned paint film, the prepared samples were subjected to the 1000-hour salt spray testing stipulated by JIS Z 2371 (5%-NaCl solution, 35°C, and pH 6.5 to 7.2), and the time was measured wherein marked outflow rust is generated, e.g., a rust pool is generated at the lower portion of the sample. Note that the dry film thickness of the paint film was measured by using an electromagnetic film thickness monitor and by observing the cross-section with microscope. The measured dry film thickness was approximately 50 μm. Table 3 shows these measurement results.

[0065] As can be understood from Table 3, the steel samples 1 through 10, and the steel samples 18 and 19, according to the present invention, exhibit toughness (Charpy impact value) of 50 J/cm² or more, elongation of 33% or more, and the yield ratio of 75% or less, regardless of whether or not annealing has been performed for the hot-rolled steel. Furthermore, these samples exhibit excellent corrosion resistance wherein outflow rust is not generated after the 1000-hour salt spray testing. On the other hand, with the steel samples 11 through 17 serving as comparative examples having the steel composition out of the scope of the present invention, at least one of the toughness, elongation, yield ratio, and corrosion resistance, does not reach the sufficient level, regardless of whether or not annealing has been performed for the hot-rolled steel.

[0066] Note that the steel was manufactured with various kinds of compositions according to the present invention using actual mass production equipment, and it has been confirmed that the steel thus manufactured has the advantages according to the present invention, as well.

Table 1

Removal depth of steel plate surface layer (μm)	Corrosion resistance of steel sheet	Corrosion resistance after painting	Cr concentration in the inside layer of steel sheet - Cr concentration in the surface layer thereof (% by mass)
5	NG	NG	4.0
8	NG	NG	2.5
10	Good	Good	1.0
14	Good	Good	0.8
20	Good	Good	0.4
40	Good	Good	0.0
80	Good	Good	0.0
110	Good	Good	0.0

Table 2

Steel No.	C	N	Si	Mn	P	S	Al	Cr	Cu	Ni	Mo	Nb	V	Notes
1	0.005	0.014	0.21	0.33	0.02	0.004	0.010	9.1	-	-	-	-	-	Present invention
2	0.007	0.005	0.22	0.25	0.03	0.006	0.020	9.5	-	-	-	-	-	Present invention
3	0.011	0.008	0.30	0.10	0.02	0.003	0.010	8.8	-	-	-	-	-	Present invention
4	0.013	0.005	0.35	0.31	0.03	0.005	0.005	8.7	-	-	-	-	-	Present invention
5	0.005	0.006	0.26	0.27	0.03	0.002	0.020	9.2	-	-	-	-	-	Present invention
6	0.005	0.007	0.25	0.35	0.02	0.004	0.010	9.1	-	-	-	-	-	Present invention
7	0.006	0.005	0.23	0.32	0.02	0.004	0.010	9.3	0.55	-	-	-	-	Present invention
8	0.008	0.003	0.22	0.26	0.02	0.005	0.020	8.5	-	0.48	-	-	-	Present invention
9	0.003	0.012	0.40	0.23	0.03	0.008	0.020	6.5	-	-	0.51	-	-	Present invention
10	0.005	0.015	0.10	0.40	0.03	0.006	0.010	8.1	0.25	0.18	0.22	-	-	Present invention
11	0.013	0.008	0.28	0.36	0.03	0.006	0.020	0.1	-	-	-	-	-	Comparative example
12	0.009	0.005	0.21	0.23	0.02	0.003	0.030	4.2	-	-	-	-	-	Comparative example
13	0.007	0.007	0.32	0.36	0.03	0.005	0.010	11.4	-	-	-	-	-	Comparative example
14	0.012	0.009	0.38	0.35	0.02	0.009	0.010	13.5	-	-	-	-	-	Comparative example
15	0.052	0.007	0.24	0.21	0.03	0.004	0.020	9.2	-	-	-	-	-	Comparative example
16	0.006	0.061	0.25	0.28	0.03	0.003	0.020	8.9	-	-	-	-	-	Comparative example
17	0.033	0.031	0.22	0.31	0.02	0.005	0.010	9.1	-	-	-	-	-	Comparative example
18	0.005	0.006	0.28	0.22	0.03	0.005	0.012	9.4	-	-	-	0.043	-	Present invention
19	0.007	0.006	0.32	0.18	0.03	0.004	0.020	9.3	0.15	0.18	-	0.060	0.05	Present invention

Table 3

Steel No.	Annealing for hot-rolled steel	Removal depth of steel sheet surface layer (μm)	Properties of hot-rolled steel (Hot-rolled annealed steel)				Properties of cold-rolled annealed steel			
			Cr concentration of surfacelayer of steel sheet (% by mass)	Cr concentration of inside layer of steel sheet (% by mass)	Time for outflow rust to occur (hour)	Charpy impact value (J/cm^2)	Elongation (%)	Yield ratio (%)	Time for outflow rust to occur (hour)	Notes
1	Yes	15	8.2	9.1	>1000	90	35	65	>1000	Present invention
2	Yes	15	8.7	9.5	>1000	120	36	63	>1000	Present invention
3	Yes	15	8.0	8.8	>1000	100	35	68	>1000	Present invention
4	Yes	15	7.8	8.7	>1000	100	35	70	>1000	Present invention
5	Yes	15	8.3	9.2	>1000	110	37	65	>1000	Present invention
6	Yes	15	8.3	9.1	>1000	120	37	66	>1000	Present invention
7	Yes	15	8.5	9.3	>1000	100	38	62	>1000	Present invention
8	Yes	15	7.7	8.5	>1000	130	36	65	>1000	Present invention
9	Yes	15	6.0	6.5	>1000	90	35	70	>1000	Present invention
10	Yes	15	7.3	8.1	>1000	80	35	68	>1000	Present invention
11	Yes	15	<0.1	0.1	80	130	40	62	100	Comparative example
12	Yes	15	3.8	4.2	350	130	39	63	400	Comparative example
13	Yes	15	11.0	11.4	>1000	30	30	77	>1000	Comparative example
14	Yes	15	13.3	13.5	>1000	20	29	80	>1000	Comparative example
15	Yes	15	8.4	9.2	>1000	20	29	78	>1000	Comparative example
16	Yes	15	8.0	8.9	>1000	20	30	76	>1000	Comparative example
17	Yes	15	8.2	9.1	>1000	30	30	77	>1000	Comparative example
1	No	15	8.3	9.1	>1000	90	34	66	>1000	Present invention
1	No	5	5.1	9.1	300	90	34	66	400	Comparative example
1	No	8	6.6	9.1	500	90	34	66	600	Comparative example

Table 3 (Continued)

Steel No.	Annealing for hot-rolled steel	Removal depth of steel sheet surface layer (μm)	Properties of hot-rolled steel (Hot-rolled annealed steel)				Properties of cold-rolled annealed steel			
			Cr concentration of surface layer of steel sheet (% by mass)	Cr concentration of inside layer of steel sheet (% by mass)	Time for outflow rust to occur (hour)	Charpy Impact value (J/cm^2)	Elongation (%)	Yield ratio (%)	Time for outflow rust to occur (hour)	Notes
2	No	15	9.1	9.5	>1000	110	36	63	>1000	Present invention
3	No	15	8.1	8.8	>1000	90	35	70	>1000	Present invention
4	No	15	8.0	8.7	>1000	100	34	71	>1000	Present invention
5	No	15	8.4	9.2	>1000	100	35	67	>1000	Present invention
6	No	15	8.5	9.1	>1000	100	37	68	>1000	Present invention
7	No	15	8.8	9.3	>1000	100	38	64	>1000	Present invention
8	No	15	7.9	8.5	>1000	90	35	70	>1000	Present invention
9	No	15	6.1	6.5	>1000	80	34	70	>1000	Present invention
10	No	15	7.5	8.1	>1000	80	34	69	>1000	Present invention
11	No	15	<0.1	0.1	40	130	39	65	50	Comparative example
12	No	15	4.0	4.2	300	120	38	65	300	Comparative example
13	No	15	11.3	11.4	>1000	20	27	82	>1000	Comparative example
14	No	15	13.5	13.5	>1000	10	26	85	>1000	Comparative example
15	No	15	8.5	9.2	>1000	10	28	82	>1000	Comparative example
16	No	15	8.2	8.9	>1000	10	28	81	>1000	Comparative example
17	No	15	8.5	9.1	>1000	20	27	81	>1000	Comparative example
18	Yes	15	8.7	9.4	>1000	210	40	62	>1000	Present invention
19	Yes	15	8.6	9.3	>1000	210	38	63	>1000	Present invention
18	No	15	9.0	9.4	>1000	200	38	63	>1000	Present invention
19	No	15	9.0	9.3	>1000	200	38	64	>1000	Present invention

Industrial Applicability

[0067] The steel according to the present invention also has the great advantage of relatively low costs. The steel according to the present invention is formed with low concentration of Cr, C, and N, as compared with SUS304 or 11%-Cr-containing stainless steel, which enables omission of annealing after hot rolling, thereby enabling further cost reduction. On the other hand, the steel according to the present invention may be applied to various kinds of structural materials such as building materials due to excellent mechanical properties and low costs thereof, and particularly, the steel according to the present invention has the advantage of use in the cold region.

[0068] The present invention provides Cr-containing steel for freezing containers, having the excellent advantages of sufficient low-temperature toughness, impact toughness, and corrosion resistance, and furthermore, has the advantage of low costs as compared with stainless steel.

Claims

1. Structural Cr-containing steel comprising:

0.002 to 0.02% by mass of C;
 0.002 to 0.02% by mass of N;
 0.05 to 1.0% by mass of Si;
 0.05 to 1.0% by mass of Mn;
 0.04% by mass or less of P;
 0.02% by mass or less of S;
 0.001 to 0.1% by mass; of Al
 6.0 to 10.0% by mass of Cr, and
 the balance being Fe and unavoidable impurities,

wherein the Cr-concentration in the surface layer of the steel is equal to or more than the value wherein 1% by mass is subtracted from the Cr-concentration within the steel.

2. Structural Cr-containing steel according to Claim 1, further comprising 0.1 to 1.0% by mass of Cu.

3. Structural Cr-containing steel according to Claim 1 or Claim 2, further comprising at least one of:

0.1 to 1.0% by mass of Ni; and
 0.1 to 1.0% by mass of Mo.

4. Structural Cr-containing steel according to any one of Claim 1 through Claim 3, further comprising at least one of:

0.005 to 0.10% by mass of Nb; and
 0.005 to 0.20% by mass of V.

5. A manufacturing method for structural Cr-containing hot-rolled steel comprising:

a step wherein a steel material comprising:

0.002 to 0.02% by mass of C;
 0.002 to 0.02% by mass of N;
 0.05 to 1.0% by mass of Si;
 0.05 to 1.0% by mass of Mn;
 0.04% by mass or less of P;
 0.02% by mass or less of S;
 0.001 to 0.1% by mass of Al;
 6.0 to 10.0% by mass of Cr; and

the balance being Fe and unavoidable impurities, is formed into a steel strip by hot rolling after reheating; wherein the steel surface is removed by a removal depth of 10 to 200 μm by descaling.

6. A manufacturing method for structural Cr-containing cold-rolled steel, wherein following said descaling processing

according to Claim 5, cold rolling, annealing cold-rolled steel, and pickling are performed.

7. A manufacturing method for structural Cr-containing steel according to Claim 5 or Claim 6, wherein said steel material further comprising Cu of 0.1 to 1.0% by mass.

8. A manufacturing method for structural Cr-containing steel according to Claim 5 or Claim 6, wherein said steel material further comprising at least one of:

0.1 to 1.0% by mass of Ni; and

0.1 to 1.0% by mass of Mo.

9. A manufacturing method for structural Cr-containing steel according to Claim 5 or Claim 6, wherein said steel material further comprising at least one of:

0.005 to 0.10% by mass of Nb; and

0.005 to 0.20% by mass of V.

10. Structural Cr-containing steel according to any one of Claim 1 through Claim 4, wherein said steel is employed for freezing containers.

11. A manufacturing method for structural Cr-containing hot-rolled steel according to Claim 5 or any one of Claim 7 through Claim 9, wherein said structural Cr-containing steel is employed for frame material of freezing containers.

12. A manufacturing method for structural Cr-containing cold-rolled steel according to Claim 6 or any one of Claim 7 through Claim 9, wherein said structural Cr-containing steel is employed for external-wall material of freezing containers.

13. A freezing container formed of said Cr-containing steel according to Claim 10, wherein formation of said freezing container is made by forming and welding, and wherein the steel surface is coated with dry-paint film thickness of 10 μm or more.

14. A freezing container formed of said Cr-containing steel manufactured with said manufacturing method according to Claim 11 or 12, wherein formation of said freezing container is made by forming and welding, and wherein the steel surface is coated with dry-paint film thickness of 10 μm or more.

15. Structural Cr-containing steel according to any one of Claim 1 through Claim 4, wherein said steel is used for civil engineering and construction.

16. A manufacturing method for structural Cr-containing hot-rolled steel according to Claim 5 or any one of Claim 7 through Claim 9, wherein said structural Cr-containing hot-rolled steel is used for civil engineering and construction.

17. A manufacturing method for structural Cr-containing cold-rolled steel according to Claim 6 or any one of Claim 7 through Claim 9, wherein said structural Cr-containing steel is used for civil engineering and construction.

FIG. 1

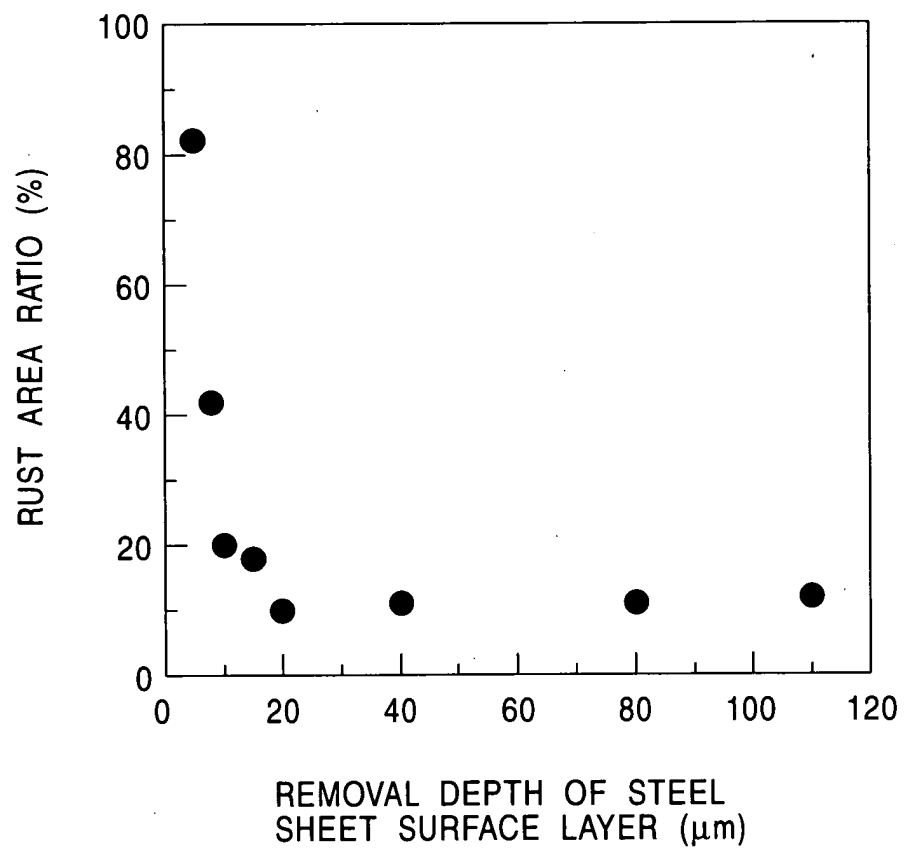
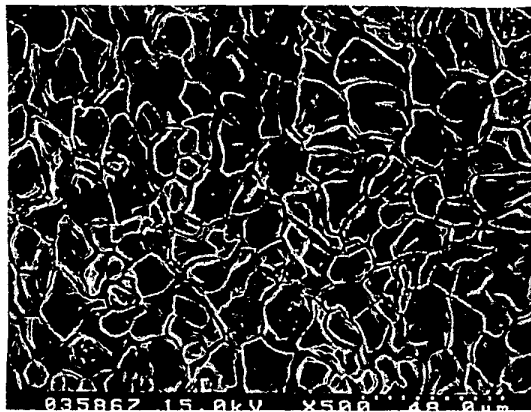


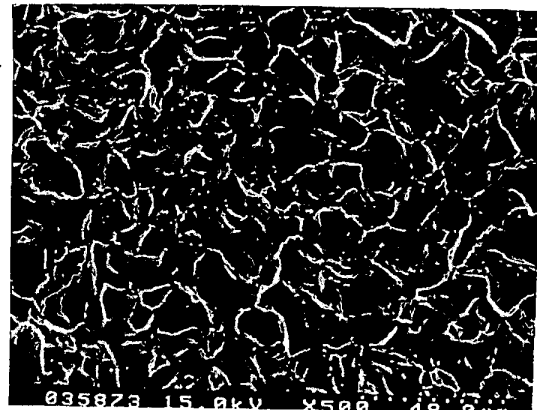
FIG. 2A



50μm

REMOVAL DEPTH OF
STEEL SHEET SURFACE
LAYER OF 8 μm

FIG. 2B



50μm

REMOVAL DEPTH OF
STEEL SHEET SURFACE
LAYER OF 40 μm

FIG. 3A

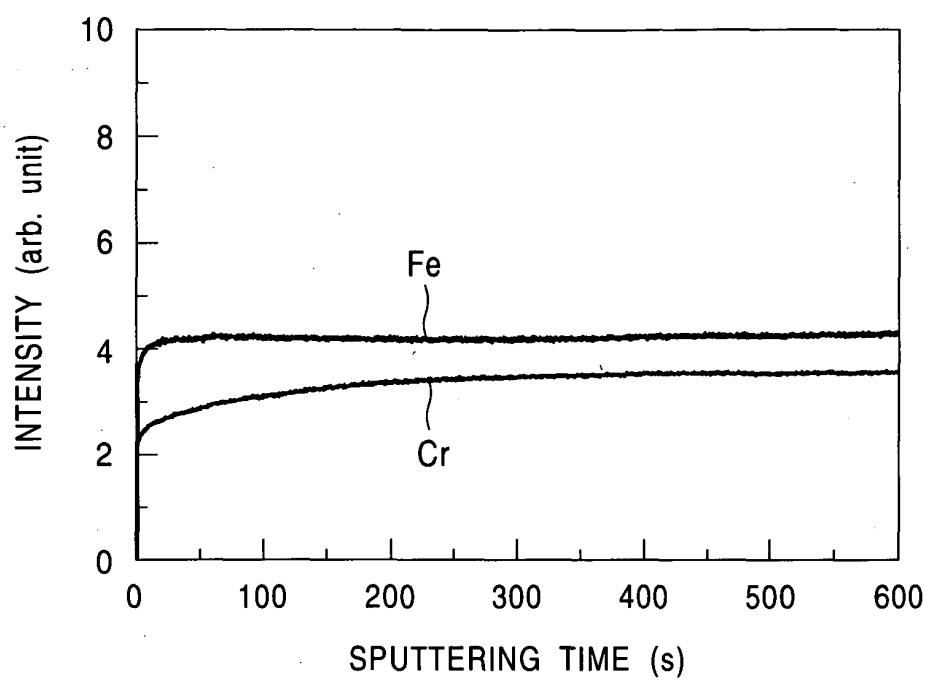


FIG. 3B

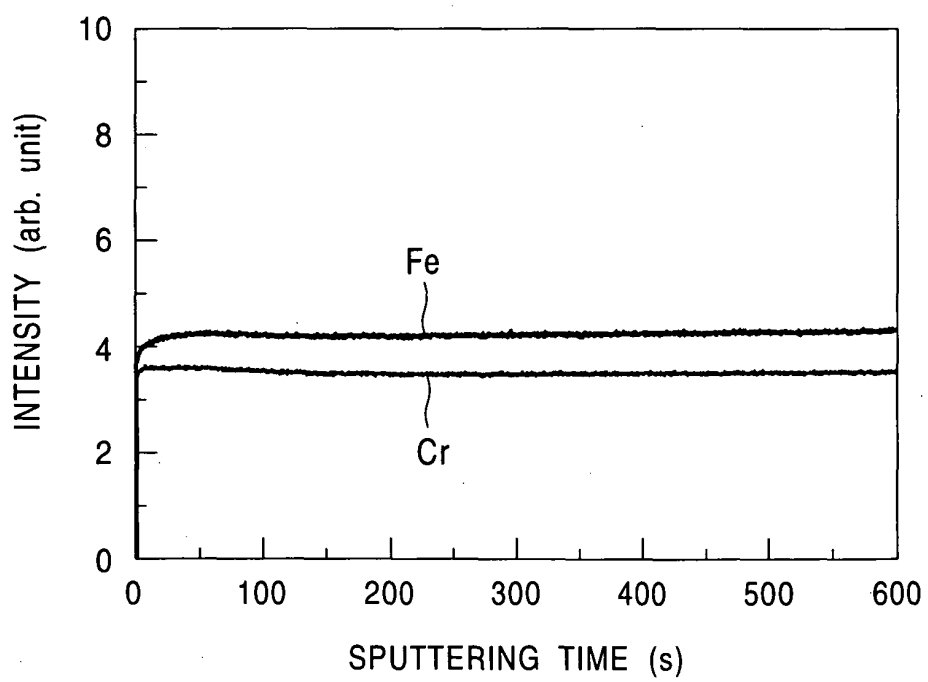
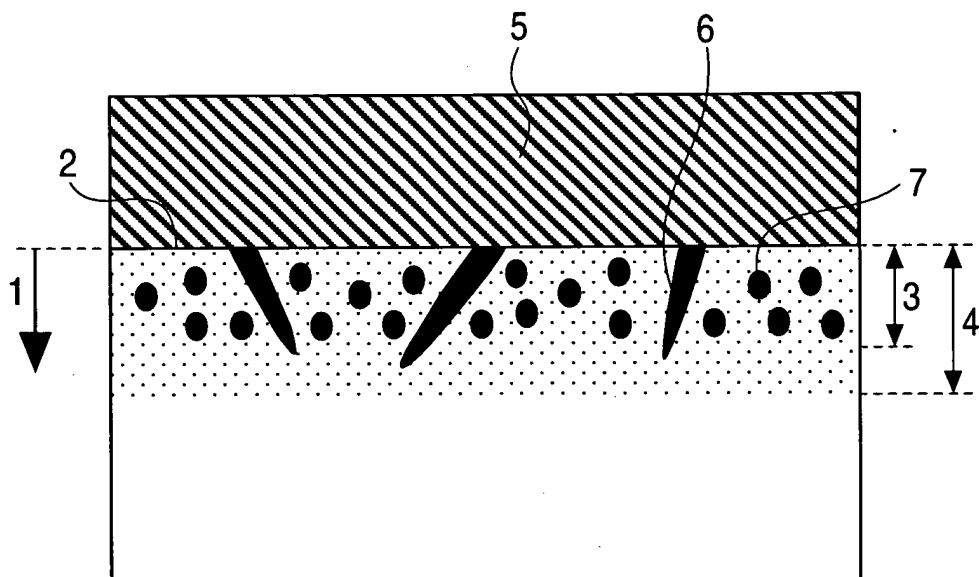


FIG. 4



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP03/10908

A. CLASSIFICATION OF SUBJECT MATTER Int.Cl ⁷ C22C38/00, 38/18, 38/48 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) Int.Cl ⁷ C22C38/00, 38/18, 38/48 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Jitsuyo Shinan Koho 1922-1996 Toroku Jitsuyo Shinan Koho 1994-2003 Kokai Jitsuyo Shinan Koho 1971-2003 Jitsuyo Shinan Toroku Koho 1996-2003 Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) WPI		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2002-161312 A (NKK Corp.), 04 June, 2002 (04.06.02), Full text (Family: none)	1-17
A	JP 8-143959 A (Nippon Steel Corp.), 04 June, 1996 (04.06.96), Par. No. [0055] (Family: none)	1-17
A	JP 10-147848 A (Nisshin Steel Co., Ltd.), 02 June, 1998 (02.06.98), Par. No. [0017] (Family: none)	1-17
☐ 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 document 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 "I" 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 18 November, 2003 (18.11.03)		Date of mailing of the international search report 02 December, 2003 (02.12.03)
Name and mailing address of the ISA/ Japanese Patent Office		Authorized officer
Facsimile No.		Telephone No.

Form PCT/ISA/210 (second sheet) (July 1998)