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- (54) Sea water corrosion resistant steel suitable for hot and wet environments and method of manufacturing the same.
- (57) A sea-water corrosion resistant steel suitable to a hot and wet environment consisting of about 0.1 wt% or less of C, 0.5 wt% or less of Si, 1.50 wt% or less of Mn, 0.005 to 0.050 wt% of Al, 0.5 to 3.50 wt% of Cr, and the balance Fe and incidental impurities.

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The present invention relates to steel that is adaptable and resistant to hot and wet environments, for example, severe environments to which ballast tanks or sea-water pipes are exposed, and to a method of manufacturing the same.

Tankers that will be manufactured in the future should have a double hull structure of the type shown in Figs. 4A and 4B to meet the regulations of the International Maritime Organization (IMO). A double hull section of a tanker 20 is used as a ballast tank 21 constructed to protect oil tanks 22. The double hull structure has the purpose of preventing oil spills.

Since the surface area of the ballast tank 21 that is exposed to sea water is considerably enlarged (two to three times) as compared with a conventional single hull structure, various problems arise in the painting process and in corrosion protection generally.

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As for problems arising in the painting process, the ballast tank 21 must be coated once or twice with coaltar epoxy resin paint. However, this is difficult and dangerous for painters because the painting operation is performed in a narrow and confined space. In addition, the considerable area to be painted causes the coating work to take a long time and to involve high cost. What is even worse, even higher cost and more labor are required for repairing the double hull structure after extended use, as compared with new ship construction.

The corrosion protection employs both paint such as coal-tar epoxy resin paint and cathodic protection measures. Since sea water flows into and out of the ballast tank 21, the ballast tank 21 is exposed to a severely corrosive environment. If sea water is present in the ballast tank 21, corrosion can substantially be prevented, thanks to modern cathodic protection measures. However, the uppermost portion of the ballast tank 21 and the underside of the deck 23 that are not normally immersed in sea water are subjected to a severely corrosive environment, the temperature of which may be very high and which is repeatedly splashed with sea water. If no water is present in the ballast tank 21, the environment becomes hot and wet and therefore the effect of cathodic protection measures cannot be obtained, and the coal-tar epoxy resin paint acts solely to prevent corrosion. The life of the coal-tar epoxy resin paint applied to the ballast tank can be expected to be about ten years, which is about half the life of the ship. In the residual ten years corrosion must be prevented by further painting, with major problems and difficulties.

Since the ballast tank is in a severely corrosive environment and the coating work under adverse conditions encounters problems, hazards and difficulties, there has been a desire for an improved steel product that is especially effective for use in a ship and which has excellent resistance against sea water corrosion under hot and wet environments.

Conventional sea-water corrosion resistant steel, an example of which has been disclosed in Japanese Patent Laid-Open No. 51-25420, is designed for use in marine structures and harbor facilities, which is sharply different from the environment faced by the steel according to the present invention; it is very different from the hot and wet environment in the ballast tank 21 where sea water flows in and out. Therefore, steel typified by the type disclosed in Japanese Patent Laid-Open No. 51-25420 contains copper as a required element. However, the steel according to the present invention should contain no copper, because copper does not resist corrosion of the ballast tank where sea water flows in and out, and even adversely affects corrosion resistance.

Steel having sea water corrosion resistance and containing no copper has been disclosed in Japanese Patent Laid-Open No. 5-302148. It contains silicon and aluminum in relatively large quantities of 0.5 to 2% and 0.5 to 3% respectively, in order to obtain ferromagnetic ferrite.

Another example of sea-water corrosion resistant steel has been disclosed in Japanese Patent Laid-Open No. 64-79346. It contains 7 to 20% aluminum. It is effective when used as a reinforcing steel when substantially no welding needs to be performed. However, it is not suitable for use where a multiplicity of welding processes are required, for example, in a ballast tank for a ship.

Although steel used to construct ships has been manufactured on the basis of component and process designs based upon strength, toughness and weldability, no means to improve corrosion resistance has been employed. In sharp contrast, the present invention provides a novel steel having excellent corrosion resistance for use in ballast tanks and sea water pipes that are subjected to severe corrosive environments.

The corrosive environment to which the ballast tank is subjected is a hot and wet environment in which sea water flows in and out. As a typical example where crude oil is transported from the Near or Middle East to Japan, the oil tanks 22 shown in Fig. 4A contain no oil during the first trip from Japan to the Near or Middle East. Without oil the ballast tank 21 is substantially filled with sea water in order to balance the ship for safe navigation. The portion of tank 21 immersed in sea water and the upper portion of the tank 21 are substantially exposed to splashing sea water. When the ship sails from the Near or Middle East to Japan, it is filled with crude oil. Sea water in the ballast tank 21 is discharged and the ballast tank 21 is empty. The space in the ballast tank at that time is exposed to a hot and wet condition by sea water left in the bottom of the ship and by heat transmitted from and through the deck. One cycle, in which the ballast tank is subjected to the foregoing cycle of corrosive environment, may be about forty days.

In conventional shipbuilding procedures the steel is welded with a large heat input by means of a so-called "single layer for one side" technique. This improves efficiency of the welding process as the tanker is built. When steel containing alloy elements is welded with a large heat input, the toughness of the welded portion deteriorates substantially as compared with usual shipbuilding welding methods.

Important objects of the present invention are to provide a special steel capable of overcoming the foregoing problems and exhibiting excellent corrosion resistance against sea water in a hot and wet environment, and to provide a method of manufacturing the same.

Another object of the present invention is to provide a new weldable steel having excellent welded portions even when welded with a large heat input. Still another object is to provide a method of manufacturing such a new steel.

We have investigated in detail the influence of alloy elements in steels. This was done by using an apparatus arranged as shown in Fig. 1 to simulate a corrosive environment. As a result, it was found that steel having a special chemical composition exhibits excellent corrosion resistance under these conditions. Furthermore, we have found that additions of REM and Ti in particular quantities enables the user to prevent deterioration of toughness in weld heat affected zones (HAZ). ("REM" means rare earth metals, in particular La or Ce, for example.) In addition, another fact was found that employment of a special and novel manufacturing method further improves corrosion resistance.

According to one aspect of the present invention there is provided a sea-water corrosion resistant steel suitable to hot and wet environments comprising about: 0.1 wt% or less of C; 0.5 wt% or less of Si; 1.50 wt% or less of Mn; 0.005 to 0.050 wt% of Al; 0.5 to 3.50 wt% of Cr; and the balance Fe and incidental impurities.

According to another aspect of the present invention, there is provided a method of manufacturing seawater corrosion resistant steel suitable to hot and wet environments comprising the steps of casting and hotrolling steel comprising about 0.1 wt% or less of C, 0.5 wt% or less of Si, 1.50 wt% or less of Mn, 0.005 to 0.050 wt% of Al, 0.5 to 3.50 wt% of Cr, and the balance Fe and incidental impurities; accelerated cooling the steel at a cooling rate of about 3 to 20°C/sec immediately after the steel has been heated due to casting and hot rolling; stopping the cooling when the steel has been cooled to about 400°C to 600°C; and cooling the steel with air.

Other and further objects, features and advantages of the invention will be appear more fully from the following description, and from the drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

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Fig. 1 is an explanatory view showing the schematic structure of a simulation testing apparatus of a ballast tank:

Fig. 2 is a graph showing effect of Cr content on corrosion weight loss of test samples;

Fig. 3 is a graph showing effect of Cr content on the maximum depth of corrosion and the average depth of corrosion of the test samples;

Fig. 4A is a plan view of a tanker having a double hull structure; and

Fig. 4B is a cross-sectional view taken along the line X-X of Fig. 4A.

An important object of the present invention is to provide a novel sea-water corrosion resistant steel composition which is resistant to hot and wet environments and is capable of reducing corrosion weight loss, and is free from local corrosion while maintaining smooth corrosive surfaces, even in an environment in which sea water and the atmosphere, the humidity of which may be as high as 100%, are repeatedly applied to the steel.

Decrease in corrosion weight loss means that generation of rust on the coated surface of a ballast tank, arranged to be protected from corrosion by coating and cathodic protection measures, can be prevented or severely curtailed. The smooth corrosive surface achieved according to this invention helps to prevent occurrence of conditions that cause concentration of distortion or metal fatigue.

The advantages of this invention can be achieved by adding effective amounts of Cr, Ni and Mo, more preferably Nb and Ti. Furthermore, restriction of precipitation of carbides after hot rolling further enhances the beneficial effects of Cr and Mo.

Another object of the present invention is to improve the toughness of portions of sea-water corrosion resistant steel exposed to a hot and wet environment and joined by welding with large heat input. Addition of effective amounts of REM, Ti and N does not reduce the toughness of the portion that has been welded with large heat input; on the contrary it improves toughness.

Effective component ranges will be described in the following paragraphs, along with reasons for determining the component ranges and reasons for using the described novel method of manufacturing the seawater corrosion resistant steel.

C: about 0.1 wt% or less

Although reduction of the addition of C will realize advantages in corrosion resistance and weldability, the upper limit of the content of C is about 0.1 wt% because C is an element that helps to determine strength.

Si: about 0.50 wt% or less

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Since the reduction of addition of Si prevents adverse influences on toughness, the upper limit of Si is about 0.50 wt%.

Mn: about 1.50 wt% or less

Although Mn is an important element that influences strength, toughness and weldability, toughness and the weldability are adversely affected if the content of Mn exceeds about 1.50 wt%. Therefore, the upper limit of the content of Mn is about 1.50 wt%.

Al: about 0.005 to 0.050 wt%

All is added to serve as a deoxidizer, and the content of All is determined to be about 0.005 to 0.050 wt% so far as weldability is not affected adversely.

Cr: about 0.50 to 3.50 wt%

The most effective element to improve corrosion resistance in the present invention is Cr. Since the contemplated corrosive environment is very severe, addition of not more than about 0.50 wt% Cr cannot significantly reduce corrosion and/or achieving a smooth corrosive surface. Since the foregoing effects can be obtained if Cr is added in an amount of about 0.50 wt% or more, the lower Cr limit is about 0.50 wt%. If the addition of Cr is increased, the effect of reducing corrosion weight loss can be attained. However, if the Cr content exceeds about 3.50 wt%, the steel surface is susceptible to a pitting corrosive state. If the quantity of Cr addition is increased to about 9 wt%, only pitting corrosion is realized, similarly to that observed on stainless steel. Since the percentage Cr at which corrosion weight loss can be reduced and a smooth corrosive surface can be formed is about 3.50 wt% or less, the upper limit is determined to be about 3.50 wt%. However, it is preferable that the quantity of Cr is about 1.2 to 3.0 wt%.

Ni: about 1.5 wt% or less

It is preferable that Ni be added together with Cr, which improves corrosion resistance. The addition of Ni improves corrosion resistance and makes the corroded surface uniform. If the quantity of Ni exceeds about 1.5%, a tendency toward strengthening and hardening the steel is attained, and problems take place regarding toughness and weldability. Therefore, the quantity of Ni is about 1.5 wt% or less.

Mo: about 0.8 wt% or less

Although addition of Mo enables a similar effect to that of Ni, excessive Mo addition is considered to raise critical problems in toughness and weldability. Therefore, the addition of Mo is determined to be about 0.8 wt% or less.

Ni + Mo: about 1.5 wt% or less

Ni and Mo enable substantially the same effect to be obtained. Since both Ni and Mo otherwise have problems of toughness and weldability, the upper limit of Ni + Mo is determined to be about 1.5 wt%.

Ti: about 0.005 to 0.05 wt%

Although Cr, Ni and Mo are elements that are effective to improve corrosion resistance, Cr and Mo readily form carbides which reduce the portion of Cr and Mo which is present in solution that effectively exhibit corrosion resistance. Since Ti is an element that forms carbides and has an affinity that is greater than those of Cr and Mo, Ti carbides are formed with priority. Therefore, forming of Cr carbides and Mo carbides is restricted

and reduction of quantity of the solid solutions of Cr and Mo can be prevented. If the quantity of Ti is about 0.005 wt% or less, the foregoing effect cannot be obtained.

Furthermore, Ti significantly contributes to toughness of the welded portion of the steel where it has been joined with large heat input, because Ti forms nitrides when it coexists with REM. However, the effect of Ti cannot substantially be obtained if the quantity is about 0.005 wt% or less. If the same is about 0.005 wt% or more, the increase of Ti causes saturation to take place gradually. If the quantity of Ti exceeds about 0.05 wt% the toughness of the base metal deteriorates. Therefore, the range is limited to about 0.005 to 0.05 wt%. When Ti coexists with REM, Ti is a required element. If REM is not present Ti may be present in the range of Nb + Ti discussed in a subsequent paragraph.

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Nb: about 0.005 to 0.05 wt%

Similarly to Ti, Nb is an element provided for forming carbides. The addition of Nb restricts forming of Cr and Mo carbides, and accordingly corrosion resistance obtainable from Cr and Mo in solution can be improved effectively. If the Nb content is about 0.005 wt% or less, the foregoing effect cannot be obtained. Since the toughness of the steel deteriorates if the content is about 0.05 wt% or more, the upper limit of Nb is determined to be about 0.05 wt%.

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Nb + Ti: about 0.005 to 0.05 wt%

Nb and Ti have similar effects of restricting precipitation of Cr carbide and Mo carbide and effectively improving corrosion resistance by enlarging the quantities of Cr and Mo in solution. However, the foregoing effects can be obtained only when the quantity of Nb + Ti is about 0.005 wt% or more. In order to improve toughness, the upper Nb + Ti limit is determined to be about 0.05 wt%.

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REM: about 0.0015 to 0.020 wt%

If REM coexists with Ti, REM significantly improves the toughness of the portion welded with a large heat input of about 100 KJ/cm or more since it enhances the effect of Ti. If the percentage of REM is less than about 0.0015 wt%, its effect cannot be obtained. If the quantity exceeds about 0.020 wt%, the toughness of the base metal deteriorates. Therefore, the optimum REM content is determined to be about 0.0015 to 0.020 wt%. As the REM, employment of La or Ce will enable a significant effect to be obtained.

N: about 0.0020 to 0.0120 wt%

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N is an element required to form TiN that is important to improve the toughness of the structure of portions welded with large heat input. In order to improve toughness, the N content must be about 0.0020 wt% or more. If the N content exceeds about 0.0120 wt%, the foregoing effect cannot be obtained and toughness sometimes deteriorates. Therefore, the N content is limited to about 0.0020 to 0.0120 wt%.

Beneficial manufacturing steps, which serve to improve the corrosion resistance of the sea-water corrosion resistant steel when exposed to a hot and wet environment, will now be described.

It is usual that steel is subjected to the usual casting and hot rolling processes. According to this invention, after hot rolling has been completed, cooling of the steel is commenced at the moment the temperature of the steel is about 900°C. Cr carbides and Mo carbides are, in this case, precipitated during the cooling process when the cooling speed is lower than about 3°C/sec. This has the effect of deteriorating the corrosion resistance obtainable from Cr and Mo in solution. Therefore, the lower limit of the cooling speed is determined to be about 3°C/sec. If the cooling speed exceeds about 20°C/sec, transformation products increase and toughness deteriorates. Therefore, the upper limit of the cooling speed is determined to be about 20°C/sec. If the temperature at which cooling is stopped after accelerated cooling has been performed, is higher than about 600°C, Cr carbides and Mo carbides are precipitated after accelerated cooling process has been completed. Therefore, improvement of corrosion resistance against sea water, obtainable from Cr and Mo in solution, deteriorates. Therefore, the upper limit of the temperature at which cooling is stopped is determined to be about 600°C. If the temperature at which cooling is stopped is lower than about 400°C, transformation products increase and toughness deteriorates. Therefore, the lower limit of the temperature at which cooling is stopped is determined to be about 400°C.

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Examples

Example 1

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Test samples having compositions shown in Table 1 were subjected to a test simulating a ballast tank of a ship. This was done by using a testing apparatus as shown in Fig. 1. Testing tank 1 was half-filled with artificial sea water 2 conforming to ASTM D1141. Each test sample 4 was immersed in the artificial sea water 2 at position 9 for one week, and then the test sample 4 was raised to position 10 in the atmosphere 3, the humidity of which was 100%, and it was allowed to stand for one week. Then the test sample 4 was immersed in the artificial sea water 2 for one week. The cycle was repeated. A drum 5, to which the test sample 4 was attached, was controlled by the rotation shaft 6 to rotate at 0.5 m/sec in either the artificial sea water or the atmosphere. Air was injected through an air-bubbling pipe 8 to cause bubbling in the lower portion of the testing tank 1 to stir the sea water and introduce oxygen into the sea water. The temperature in the testing tank was controlled by a heater 7. Since the cover portion of the testing tank 1 was substantially closed tightly, the difference between the temperature of the artificial sea water and that of the atmosphere was 1°C or less and the humidity of the atmosphere was about 100%. A corrosion resistance test was performed. Five cycles were performed each of which consisted of immersion in 40°C artificial sea water for one week and allowing to stand in the atmosphere the humidity of which was 100% and the temperature of which was 40°C. The test sample 4 was manufactured by heating the material to 1150°C for one hour and then it was hot-rolled, followed by air cooling (at a cooling speed of 0.5°C/sec).

Results of measurement of the corrosion weight loss of the test samples, evaluation of the condition of the corrosive surface and measurement of the depth of corrosion are shown in Table 2. The corrosion depth was measured such that depths of 10 places were measured in a descending order by using a depth gauge. The maximum corrosion depth and the average corrosion depth were shown. After the test, rust was removed and the condition of the corrosive surface was evaluated from the viewpoint of smoothness of the surface. The surfaces each having a uniform corrosive condition with slightly uneven surface were evaluated as satisfactory as indicated by the symbol " \bigcirc ". The surfaces each having a uniform corrosive condition with a rather largely uneven surface condition and those having a largely uneven surface with a small number of shallow pits were indicated by the symbol " \bigcirc " and " \triangle ", respectively. The surfaces having a largely uneven surface with a large number of deep pits were evaluated as unsatisfactory as indicated by the symbol "x". Fig. 2 shows the quantity of corrosion with respect to Cr content, and Fig. 3 shows the depth of corrosion with respect to Cr content. As comparative examples, conventional steel KA36 for ships conforming to the NK (Nihon Kaiji Associates) standard was simultaneously tested. The results of the tests were as follows.

(1) Corrosion Weight Loss

When the quantity of Cr added was increased corrosion weight loss was decreased. When the quantity was 5 to 6 wt%, corrosion weight loss is increased. When the quantity of Cr added was further increased, corrosion weight loss decreased.

The quantity of corrosion (mg/cm³) were obtained using the difference between the quantity of initial weight of the test piece and the weight of the test piece from which the rust was removed by the above-mentioned corrosion test and the difference was computed in terms of a unit surface area of a test piece. Mean reduction quantity of plate thickness at one side (mm) was computed using quantity of corrosion.

(2) Corrosion Depth and Condition of Corrosion

The depth of corrosion is decreased as compared with the comparative material KA36 when the quantity of Cr addition was about 3 to 4 wt%. When the quantity of Cr addition was enlarged, both maximum depth of corrosion and the average depth of corrosion were enlarged. When Cr content was 3.5 wt% or less, the surface was brought to a uniform corrosive state. When the quantity of Cr was enlarged from the foregoing state, a locally corrosive state was realized. Comparative steel examples 2 to 4 were brought to a locally corrosive state. The locally corrosive state raised a problem in use, such that stress concentration took place. The range of the quantity of addition of Cr in which corrosion weight loss could be prevented satisfactorily, and a smooth corrosive surface could be formed, was 3.5 wt% or less. When Cr content was less than about 0.5 wt%, a satisfactory effect was not obtained.

Examples 2, 3 and 4

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The composition of a test sample is shown in Table 3. Results of measurement of corrosion weight loss of the test samples, evaluation of the state of the corrosive surface and measurement of the depth of corrosion are shown in Table 4.

The composition of another test sample is shown in Table 5. Results of measurement of corrosion weight loss of the test samples, evaluation of the state of the corrosive surface and measurement of the depth of corrosion are shown in Table 6.

The composition of another test sample is shown in Table 7. Results of measurement of corrosion weight loss of the test samples, evaluation of the state of the corrosive surface and measurement of the depth of corrosion are shown in Table 8.

The method of manufacturing the test sample, the test method, the evaluation method and testing conditions for the corrosion resistance test were the same as those according to Example 1.

The range of the quantity of addition of Cr in which corrosion weight loss of the steel was prevented satisfactorily, and a smooth corrosive surface was formed, was about 0.5 to 3.5 wt% or less similarly to Example 1.

Table 4 shows the results of comparisons between example steel and comparative example steel when the quantity of Cr was about the same. Example steel 1 to 3 and comparative example steel 1 each contained Cr 1 wt%. Example steel 4 to 6 and comparative example steel 2 each contained Cr 2 wt%. Example steel 7 and comparative example steel 3 each contained Cr 3 wt%. As the quantity of Ni + Mo increased, corrosion weight loss and corrosion depth were decreased and projections and pits in the corrosive surface were restricted so that a uniform corrosive state was realized. In particular, the additions of Ni and Mo were effective to reduce corrosion weight loss. As can be understood from results of comparison between example steel 4, 5 and 6 and comparative example steel 4, 5 and 6, the toughness deteriorated when Ni and Mo were not included in the adequate range.

Table 6 shows the results of comparisons between example steel and comparative example steel. Example steel 1 and comparative steel sample 1 each contained Cr 0.7 wt%. Example steel 2 and 3 and comparative steel 2 each contained Cr by wt%. Example steel 4 and 5 and comparative example steel 3 and 4 each contained Cr 2 wt%. Example steel 6 and comparative example steel 5 each contained Cr 3.4 wt%. As the quantity of Nb + Ti increased, corrosion weight loss and corrosion depth were decreased.

As can be understood from comparison between example steel 4 and 5 and comparative example steel 6, 7 and 8, the toughness of the base metal deteriorated when the additions of Nb and Ti were large.

Table 8 shows the results of comparisons between example steel and comparative example steel that contained Cr in the same quantity. As described above, the additions of Ni, Mo, Nb and Ti decreased corrosion weight loss and corrosion depth.

Example 5

When welding with a large heat input is performed, the toughness of the heat affected zone of the joint portion of welding is an important factor. Therefore measurements were performed to evaluate the toughness of simulated heat affected zone of a variety of sea-water corrosion resistant steel. In this case, heat cycle corresponds to the same which the joint portion of welding by a large heat input was subjected. In addition, the steel was subjected to a corrosive test using a sea-water corrosion resistance testing tank that was capable of simulating the hot and wet environment. The method of the corrosion resistance test, the evaluation method and the testing conditions were the same as those according to Example 1.

The components of test samples corresponding to claim 5 are shown in Table 9.

Table 10 shows the results of Charpy impact tests, to which a heat affected zone was subjected after a simulated heat cycle corresponding to the heat hysteresis of submerged arc welding of 100 KJ/cm in the manner of the single layer for one side. The results are shown together with the results of Charpy impact tests to which the base metal was subjected.

Table 11 shows corrosion weight loss and corrosion depth resulting from the sea-water corrosion resistance test.

Table 11 shows the results of comparison between the results of the sea-water corrosion resistance test to which the example steel and the comparative example steel were subjected. They contained the same quantity of Cr.

According to the results shown in Table 10, the limitations of REM, Ti and N to the ranges according to the present invention significantly improved the toughness of the joint portion welded with a large heat input as compared with the comparative example steel such that toughness exhibiting absorbed energy (vEo) ex-

ceeding the value of KA36 was obtained.

As can be understood from the results of the corrosion resistance test shown in Table 11, the limitation of the quantity of Cr to the determined range enabled corrosion resistance similar to that of the comparative example steel to be obtained even if REM and N were added. Therefore, it can be understood that the additions of REM, Ti and N did not adversely affect the corrosion resistance.

Examples 6, 7 and 8

The compositions of the test samples are shown in Table 12 and Table 15.

The results of Charpy impact tests, to which a heat affected zone was subjected after a simulated heat cycle corresponding to the heat hysteresis of submerged arc welding of 100 KJ/cm in the manner of the single layer for one side are shown in Table 13 and Table 17 together with the results of a Charpy impact test to which the base metal was subjected. The results of the corrosion resistance test against sea water are shown in Table 14 and Table 16. The method of the corrosion resistance test, the evaluation method and the testing conditions were the same as those according to Example 1. According to the results shown in Tables 13 and 17, the limitations of REM, Ti and N to the ranges according to the present invention significantly improved the toughness of the joint portion welded with a large heat input as compared with the comparative example steel such that toughness exhibiting absorbed energy (vEo) exceeding the value of KA36 was obtained.

As shown in the results of the corrosion resistance test shown in Tables 14 and 16, corrosion resistance equivalent to or somewhat superior to that of the comparative example steel can be improved if the quantities of Cr, Mo and Ni are in the limited ranges. Thus, the additions do not adversely affect the corrosion resistance obtainable from the additions of Nb and Ti.

Example 9

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As test samples, there was used example steel 2, 3 and 4 (having the same composition as those shown in Table 1) according to an example of the present invention and comparative example steel manufactured such that material having the same composition as those of conventional steel KA36 was heated to 1150°C, hot-rolled and then cooled under the conditions shown in Table 18. Test samples thus obtained were subjected to a corrosion resistance test by using the testing apparatus used in Example 1. The method, the evaluation method and testing conditions of the corrosion resistance test were the same as those of Example 1. The results of the measurements of corrosion weight loss, those of the evaluations of the corrosive surfaces, the results of the measurements of the depths of corrosion, and the results of the Charpy impact test, to which the base metal was subjected, are shown Table 19.

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(1) Corrosion Weight Loss

Corrosion weight loss was reduced due to the addition of Cr as compared with conventional steel KA36 (as realized in Example 1). Further, corrosion weight loss was further decreased by employing the manufacturing conditions included within the scope of the present invention. Also the depth of corrosion was decreased by manufacturing the steel under the conditions included within the scope of the present invention.

(2) Toughness

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Toughness did not deteriorate even if the steel was manufactured under the conditions included within the scope of the present invention. If the cooling speed exceeded the upper limit or if the temperature at which cooling was stopped was lower than the lower limit, the absorbed energy (vEo) was decreased and the toughness deteriorated.

Examples 10, 11 and 12

Test samples obtained from the test materials manufactured under the conditions shown in Table 18 were subjected to the corrosion resistance test by using testing apparatus the same as that used in Example 1. The results of the measurements of corrosion weight loss, those of the evaluations of the corrosive surfaces, the results of the measurements of the depths of corrosion, and the results of the Charpy impact test, to which the base metal was subjected, are shown Table 20, Table 21 and Table 22. Example steel 7 shown Table 20 was the same as those shown in Table 3. Example steel 6 shown Table 21 had the same composition as those shown in Table 5. Example steel 6 shown in Table 22 had the same composition as those shown in Table 7.

The method, the evaluation method and the testing conditions for the corrosion resistance test were the same as those according to Example 1.

The employment of the conditions for manufacturing the steel within the scope of the present invention enabled corrosion weight loss to be decreased. Also the depth of corrosion was decreased by employing manufacturing conditions included within the scope of the present invention. Even if the manufacturing conditions within the scope of the present invention were employed, the toughness did not deteriorate. When the cooling speed exceeded the upper limit or if the temperature at which cooling was stopped was lower than the lower limit, the absorbed energy (vEo) was decreased and the toughness deteriorated.

Examples 13, 14, 15 and 16

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The compositions of the test materials are shown in Table 23. The test materials were heated to 1150°C, hot-rolled and then cooled at 900°C under the conditions shown in table 18 so that the test samples were manufactured. The test samples obtained from the test materials were subjected to a corrosion resistance test by using the testing apparatus the same as that used in Example 1. The method, the evaluation method and the testing conditions for the corrosion resistance test were the same as those according to Example 1.

The results of measurements of corrosion weight loss, those of evaluation of the corrosive surfaces and the results of measurements of the depths of corrosion are shown in Table 24.

Table 25 shows the results of a Charpy impact test, to which heat affected zone was subjected after a simulated heat cycle corresponding to the heat hysteresis of a submerged arc welding of 100 KJ/cm in a manner of the single layer for one side, the results being shown together with the results of Charpy impact tests to which the base metal was subjected.

The employment of the conditions for manufacturing the steel within the scope of the present invention enables corrosion weight loss to be decreased. Also the depth of corrosion can be decreased by employing the manufacturing conditions included within the scope of the present invention. Even if the manufacturing conditions within the scope of the present invention were employed, the toughness of the base metal and that of the simulated heat affected zone did not deteriorate.

As described above, the sea-water corrosion resistant steel suitable to a hot and wet environment according to the present invention has excellent corrosion resistance when it is adapted to a ballast tank or a sea water pipe for a ship that is subjected to a severe corrosive environment. As a result, a contribution to making a ship maintenance-free of the ship and safety of the ship can be provided and maintained.

Furthermore, the welding with a large heat input can be employed and therefore a tanker can be built in an efficient welding manner, and the toughness of the portions joined by welding can be improved.

Although the invention has been described with reference to its preferred forms, with a certain degree of particularity, it is understood that the present disclosure of the preferred form can be changed in the details of construction. Further, various combinations and arrangements of parts may be resorted to without departing from the spirit and the scope of the invention as hereinafter claimed.

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Table 1

					<u> </u>		
Type of Steel	ပ	Si	Mn	Ωų	Ø	Ç	41
Example Steel 1	90.0	0.31	1.42	0.020	0.005	0.68	0.025
Example Steel 2	90.0	0.32	1.40	0.020	500.0	1.01	0.020
Example Stool 3	0.05	0.30	1.45	0.020	0.005	2.04	0.021
Example Steel 4	0.05	0.31	1.40	0.020	0.005	2.98	0.022
Example Steel 5	0.05	0.32	1.38	0.020	0.005	3.41	0.025
Comparative Example Steel 1	90.0	0.30	1.40	0.020	500.0	0.45	070'0
Comparative Example Steel 2	0.05	0.31	1.40	0.020	0.005	3.78	0.024
Comparative Example Steel 3	0.05	0.32	1.40	0.020	0.005	5.10	0.020
Comparative Example Steel 4	0.05	0.33	1.39	0.022	0.005	6.07	0.023
Comparative Example Steel 5	0.05	0.31	1.40	0.022	0.005	9.05	0.025
Comparative Example Steel 6	0.05	0.32	1.38	0.020	0.005	13.10	0.022
KA36	0.10	0.34	1.42	0.017	0.002	0.02	0.023

Table 2

			40°C x 5 Cycles			
i i		Corrosion Weight Loss	Loss	ď	Depth of Corrosion	sion
lype of Steel	Weight Loss (mg/cm ²)	Average Decrease in Thickness (One Side, mm)	Ratio with Respect to Comparative Example KA36 (1)	Maximum Depth of Corrosion	Average Depth of Corrosion (mm)	Evaluation of Corrosive Surface
Example Steel 1	74	0.094	62	0.42	0.36	0
Example Steel 2	72	0.092	2.2	64.0	0.31	0
Example Steel 3	57	0.073	61	98.0	0.24	0
Example Steel 4	35	0.045	37	0.33	0.25	0
Example Steel 5	34	0.043	36	0.45	0.31	0
Comparative Example Steel 1	83	0.106	88	0.52	0.39	۷
Comparative Example Steel 2	32	0.041	34	0.51	0.36	۷
Comparative Example Steel 3	38	0.048	40	64.0	0.36	×
Comparative Example Steel 4	43	0.055	9 7	0.55	0.48	×
Comparative Example Steel 5	30	0.038	32	0.69	0.61	×
Comparative Example Steel 6	9	0.008	6	1.09	0.81	×
KA36	94	0.120	100	0.50	0.41	۵

©: a uniform corrosive condition with slightly uneven surface O: a uniform corrosive condition with a rather largely uneven surface A: a largely uneven surface with a small number of shallow pits X: a largely uneven surface with a large number of deep pits

Table 3

T	,	į								
Type of Steel	ت	ī,	m u	p.,	so.	A1	#5	Ţ	ω	Ni +Mo
Example Steel 1	90.0	0.31	1.42	0.014	0.004	0.022	1.02	0.42	0.15	0.57
Example Steel 2	90.0	0.32	1.43	0.010	0.003	0.023	1.02	0.80	0.27	1.07
Example Steel 3	90.0	0.30	1.40	0.011	0.004	0.025	1.03	1.20	,	1.20
Example Steel 4	0.05	0.31	1.42	0.009	0.004	0.022	2.02	0.42	0.21	0.63
Example Steel 5	0.05	0.32	1.40	0.009	0.004	0.025	2.02	0.84	0.44	1.28
Example Steel 6	0.05	0.33	1.42	0.008	0.004	0.022	2.01		0.60	0.60
Example Steel 7	0.05	0.35	1.41	0.010	0.003	0.023	3.00	0.40	0.15	0.55
Comparative Example Steel 1	90.0	0.32	1.40	0.020	0.005	0.020	1.01	1	,	0.00
Comparative Example Steel 2	0.05	0.30	1.45	0.020	0.005	0.021	2.04	1	1	0.00
Comparative Example Steel 3	0.05	0.31	1.40	0.020	0.005	0.022	2.98	1	ı	0.00
Comparative Example Steel 4	0.05	0.33	1.41	0.008	0.004	0.021	2.02	1.78	1	1.78
Comparative Example Steel 5	0.05	0.30	1.39	0.009	0.005	0.025	2.02	ı	1.02	1.02
Comparative Example Steel 6	0.05	0.31	1.40	0.008	0.004	0.022	2.01	1.80	1.00	2.80
KA36	0.10	0.34	1.42	0.017	0.002	0.023	0.02	0.01	0.01	0.02

	Absorbed	Energy	(Base Metal) (J)					270	265	270				240	245	200	260
		d	Evaluation of Corrosive Surface	0	0	0	0	0	0	0	0	0 1 0	0	0	0	0	٥
		Depth of Corrosion	Average Depth of Corrosion (mm)	0.31	0.29	0.28	0.31	0.24	0.23	0.24	0.24	0.27	0.27	0.24	0.25	0.23	0.41
	les	Q	Maximum Depth of Corrosion (mm)	0.42	0.40	0.38	0.43	0.34	0.32	0.35	0.36	0.30	0.33	0.32	0.35	0.31	05.0
Table 4	40°C × 5 Cycles	Loss	Ratio with Respect to Comparative Example KA36 (1)	69	62	59	7.7	51	67	52	61	33	37	50	53	49	100
		Corrosion Weight Loss	Average Decrease in Thickness (One Side, mm)	0.083	0.074	0.070	0.092	0.061	0.059	0.062	0.073	0.039	0.045	090.0	0.064	0.059	0.120
			Weight Loss (mg/cm ²)	65	58	55	72	78	97	49	57	31	35	47	50	46	94
		E E	Taba or accer	Example Steel 1	Example Steel 2	Example Steel 3	Comparative Example Steel 1	Example Steel 4	Example Steel 5	Example Steel 6	Comparative Example Steel 2	Example Steel 7	Comparative Example Steel 3	Comparative Example Steel 4	Comparative Example Steel 5	Comparative Example Steel 6	KA36

©: a uniform corrosive condition with slightly uneven surface O: a uniform corrosive condition with a rather largely uneven surface Δ : a largely uneven surface with a small number of shallow pits

Table 5

Type of Steel	υ	S1	Mn	Δı	S	Cr	A1	Nb	Ţį	Nb+Ti
Example Steel 1	90.0	0.31	1.40	0.021	0.005	0.70	0.023	0.021	0.026	0.047
Example Steel 2	90.0	0.32	1.39	0.020	0.005	1.01	0.023	0.020	ſ	0.020
Example Steel 3	0.06	0.10	1,41	0.020	500.0	1.05	0.024	1	0.030	0.030
Example Steel 4	0.05	0.30	1,40	0.020	500.0	2.00	0.023	0:030	0.015	0.045
Example Steel 5	0.05	0.31	1.40	0.020	500.0	2.00	0.023	0.020	0.020	0.040
Example Steel 6	0.05	0.32	1.38	0.020	900.0	3.35	0.024	0.025	0.020	0.045
Comparative Example Steel 1	90.0	0.31	1.42	0.020	0.005	0.68	0.025	,	1	0
Comparative Example Steel 2	0.06	0.32	1.40	0.020	500.0	10.1	070.0	,	1	0
Comparative Example Steel 3	0.05	0.30	1.45	0.020	0.005	5.04	0.021	-	1	0
Comparative Example Steel 4	0.05	0.31	1.41	0.020	0.005	7.04	0.021	0.003	1	0.003
Comparative Example Steel 5	0.05	0.32	1,38	0.020	0.005	3.41	0.024	1	-	0
Comparative Example Steel 6	0.05	0.30	1.40	0.019	0.005	2.00	0.024	090.0	-	0,060
Comparative Example Steel 7	0.05	0.31	1.41	0.020	0.004	2.01	0.023		0.065	0.065
Comparative Example Steel 8	0.05	0.32	1.42	0.020	0.005	2.00	0.023	0.030	0:030	090.0
KA36	0.10	0.34	1.42	0.017	0.002	0.02	0.023	ı	ţ	0

Table 6

Absorbed Energy	vEo (Base Metal)	(J)						300	295					245	246	247	260
	a	Evaluation of Corrosive Surface	© - 0	0	0	0	0	0	©	0	0	0	0	0	0	0	٧
	Depth of Corrosion	Average Depth of Corrosion (mm)	0.29	90.36	0.24	0.23	0.31	0.24	0.22	0.24	0.25	0.30	0.31	0.24	0.24	0.25	0.41
cles	Q	Maximum Depth of Corrosion (mm)	07*0	0.42	0.35	0.35	0.43	0.31	0.32	98*0	0.33	0.45	0.45	0.32	0.33	0.33	05.0
40°C × 5 Cycles	Loss	Ratio with Respect to Comparative Example KA36 (1)	69	67	9	79	2.2	52	55	61	09	32	36	53	53	53	100
	Corrosion Weight Loss	Average Decrease in Thickness (One Side, mm)	0.083	0.094	0.076	0.074	0.092	0.062	0.066	0.073	0.071	0.038	0.043	0.064	0.064	0.064	0.120
		Weight Loss (mg/cm ²)	6.5	7.4	09	95	7.2	64	52	57	95	30	78	50	05	05	76
	1	Type of Steel	Example Steel 1	Comparative Example Steel 1	Example Steel 2	Example Steel 3	Comparative Example Steel 2	Example Steel 4	Example Steel 5	Comparative Example Steel 3	Comparative Example Steel 4	Example Steel 6	Comparative Example Steel 5	Comparative Example Steel 6	Comparative Example Steel 7	Comparative Example Steel 8	KA36

©: a uniform corrosive condition with slightly uneven surface O: a uniform corrosive condition with a rather largely uneven surface A: a largely uneven surface with a small number of shallow pits

Table 7

Type of Steel	υ	Si	Μ'n	Д.	w	A1	Cr	ŦN	Mo	Ni.+Mo	Nb	Ţį	Nb+Ti
Example Steel 1	0.06	0.31	1.39	0.010	0.005	0.023	1.00	0.78	0.24	1.02	0.010	0.015	0.025
Example Steel 2	90.0	08.0	1.40	0.011	0.005	0.024	1.03	1.16	1	1.16	0.011	0.012	0.023
Example Steel 3	90.0	0.32	1.41	0.010	0.005	0.025	1.01	0.75	0.20	0.95	-	0.020	0.020
Example Steel 4	0.05	0.31	1.42	0.010	0.004	0.020	2.05	0.82	0,40	1.22	0.012	0.010	0.022
Example Steel 5	0.05	0.31	1.41	0.010	0.004	0.022	2.02	-	0.58	0.58	0.030		0.030
Example Steel 6	0.05	0.32	1.43	0.010	0.003	0.025	3.01	0.39	0.15	0.54	0.010	0.010	0.020
Comparative Example Steel 1	90.0	0.31	1.42	0.014	0.004	0.022	1.02	0.42	0.15	0.57	1		0
Comparative Example Steel 2	90.0	0.32	1.43	0.010	0.003	0.023	1.02	08.0	0.27	1.07	'		0
Comparative Example Steel 3	90.0	0.30	1.40	0.011	0.004	0.025	1.03	1.20		1.2	1	-	0
Comparative Example Steel 4	90.0	0.31	1.40	0.010	0.005	0.023	1.00	0.78	0.27	1.05	0.004		0.004
Comparative Example Steel 5	0.05	0.32	1.40	0.009	0.004	0.025	2.02	0.84	0.44	1.28	-		0
Comparative Example Steel 6	0.05	0.30	1.39	0.008	0.004	0.022	2.01	,	09.0	9.0			0
Comparative Example Steel 7	0.05	0.31	1.41	0.009	0.004	0.022	2.01	0.42	0.19	0.61	١	0.003	0.003
Comparative Example Steel 8	0.05	0.35	1.41	0.010	0.003	0.023	3.00	0.40	0.15	0.55	-		0
KA36	01.0	0.34	1.42	0.017	0.002	0.02	0.023	١.	-	0	-	-	0

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Table 8

			40°C × 5 Cycles	cles		
, ,		Corrosion Weight Loss	Loss	Ď	Depth of Corrosion	ď
Type of Steel	Weight Loss (mg/cm ²)	Average Decrease in Thickness (One Side ,mm)	Ratio with Respect to Comparative Example KA36 (1)	Maximum Depth of Corrosion (mm)	Average Depth of Corrosion (mm)	Evaluation of Corrosive Surface
Example Steel 1	54	690.0	57	0.31	0.24	©
Example Steel 2	51	0.065	54	0.32	0.22	0
Example Steel 3	52	0.066	55	0.33	0.23	0
Comparative Example Steel 1	65	0.083	69	0.42	0.31	0
Comparative Example Steel 2	58	0.074	62	0.40	0.29	0
Comparative Example Steel 3	55	0.070	59	0.38	0.28	0
Comparative Example Steel 4	58	0.074	62	0.37	0.29	0
Example Steel 4	38	0.048	40	0.31	0.21	0
Example Steel 5	43	0.055	46	0.30	0.21	0
Comparative Example Steel 5	46	0.059	49	0.32	0.23	0
Comparative Example Steel 6	49	0.062	52	0.35	0.25	0 - 0
Comparative Example Steel 7	49	0.062	52	0.35	0.26	0 - 0
Example Steel 6	27	0.034	29	0.30	0.26	O
Comparative Example Steel 8	31	0.039	33	0.30	0.27	O - @
KA36	94	0.120	100	0.50	0.41	٧

@: a uniform corrosive condition with slightly uneven surface O: a uniform corrosive condition with a rather largely uneven surface A: a largely uneven surface with a small number of shallow pits

Table 9

Type of Steel	υ	Si	Mn	Ω4	s	C _I	A1	REM	Ţĩ	z
Example Steel 1	0.05	0.32	1.40	0.020	0.005	2.02	0.021	0.008	0.010	0.0032
Example Steel 2	0.05	0.31	1.39	0.020	0.005	3.01	0.022	0.007	0.008	0.0028
Example Steel 3	50.0	0.30	1.38	0.020	0.005	1,98	0.020	0.010	0.020	0.0035
Comparative Example Steel 1	90.0	0.30	1.39	0.021	0.004	1.95	0.021	0.025	0.012	0.0033
Comparative Example Steel 2	50.0	0.31	1.40	0.020	0.005	2.98	0.022	0.027	0.005	0.0028
Comparative Example Steel 3	50.0	0.32	1.42	0.022	0.006	1.92	0.021	0.014	0.056	0.0033
Comparative Example Steel 4	50.0	0.30	1.45	0.020	0.005	2.04	0.021	ı	ı	0.0030
Comparative Example Steel 5	0.05	0.31	1.39	0.020	0.005	2.98	0.022	ſ	0.020	0.0030
KA36	0.10	0.34	1.42	0.017	0.002	0.02	0.023	1	1	0.0050

Table 10

	Base Metal	Simulated Heat Affected Zone (HAZ)
Type of Steel	Charpy Impact Test	Charpy Impact Test
	Absorbed Energy vEo (J)	Absorbed Energy vEo
Example Steel 1	299	138
Example Steel 2	291	122
Example Steel 3	305	145
Comparative Example Steel 1	265	86
Comparative Example Steel 2	201	78
Comparative Example Steel 3	280	85
Comparative Example Steel 4	270	38
Comparative Example Steel 5	243	16
KA36	260	121

Table 11

			40°C × 5 Cycles	rcles		
		Corrosion Weight Loss	8	α	Depth of Corrosion	
Type of Steel	Weight Loss (mg/cm²)	Average Decrease in Thickness (One Side,mm)	Ratio with Respect to Comparative Example KA36 (1)	Maximum Depth of Corrosion (mm)	Average Depth of Corrosion (mm)	Evaluation of Corrosive Surface
Example Steel 1	56	0.071	09	0.36	0.24	0
Example Steel 3	55	0.070	59	0.35	0.23	0
Comparative Example Steel 1	55	0.070	59	0.37	0.24	0
Comparative Example Steel 3	53	0.068	56	0.33	0.22	0
Comparative Example Steel 4	57	0.073	61	0.36	0.24	6
Example Steel 2	34	0.043	36	0.32	0.24	0
Comparative Example Steel 2	35	0.045	37	0.33	0.25	0
Comparative Example Steel 5	35	0.045	37	0.33	0.25	0
KA36	94	0.120	100	0.50	0.41	۵

 $\circledast\colon$ a uniform corrosive condition with slightly uneven surface $\Delta\colon$ a largely uneven surface with a small number of shallow pits

Table 12

	028	035	050	050	050
	0.0028	0.0035	0.0050	0.0050	0.0050
Ţį	0.008	0.020	,	'	,
REM	0.81 0.007	0.010		1	,
Ni+Mo	0.81	0.61	1.07	0.63	0.02
Жо	ı	0.20	0.27	0.21	0.01
Ŋï	0.81	0.41	1.02 0.80 0.27 1.07	0.004 0.022 2.02 0.42 0.21	0.01
Cr	1.05	2.03	1.02	2.02	0.02
A1	0.004 0.021 1.05 0.81	0.025	0.023	0.022	0.023
တ	0.004	0.004	0.003	0.004	0.002 0.023 0.02
e4	600.0	1.43 0.009	0.010	0.009	0.34 1.42 0.017
Μn	0.32 1.42	1.43	1.43	0.31 1.42	1.42
Sŧ	0.32	0.33	0.32	0.31	78.0
ນ	90.0	0.05	90.0	0.05	0.10
Type of Steel	Example Steel 1	Example Steel 2	Comparative Example Steel 1	Comparative Example Steel 2	KA36

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Table 13

	Base Metal	Simulated Heat Affected Zone (HAZ)
Type of Steel	Charpy Impact Energy	Charpy Impact Test
	Absorbed Energy vEo (J)	Absorbed Energy vEo (J)
Example Steel 1	312	140
Example Steel 2	282	130
Comparative Example Steel 1	238	50
Comparative Example Steel 2	270	40
KA36	260	121

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Table 14

			40°C x 5 Cycles	89		
		Corrosion Weight Loss	880	Ď	Depth of Corrosion	
Type of Steel	Weight Loss (mg/cm ²)	Average Decrease in Thickness (One Side,mm)	Ratio with Respect to Comparative Example KA36	Maximum Depth of Corrosion (mm)	Average Depth of Corrosion (mm)	Evaluation of Corrosive Surfaca
Example Steel 1	57	0.073	61	0.39	0.28	0
Comparative Example Steel 1	58	0.074	62	0.40	0.29	0
Example Steel 2	46	0.059	49	0.32	0.23	©
Comparative Example Steel 2	48	0.061	51	0.34	0.24	©
KA36	94	0.120	100	0.50	0.41	∢

@: a uniform corrosive condition with slightly uneven surface O: a uniform corrosive condition with a rather largely uneven surface A: a largely uneven surface with a small number of shallow pits

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Steel	υ	Şï	甁	P4	တ	Cr.	ŊŦ	Мо	N±+Mo	A1	REM	Ti	Z

Table 15

Type of Steel														
	ပ	Şi	M	ρ,	တ	Cr	N£	Мо	N±+Mo	Al	REM	ŢŢ	N.	z
Example Steel 1 0	0.05	0.32	1.42	0.020	0.005	2.02	1	ı	00.0	0.021	0.008	0.01	0.020	0.0032
Example Steel 2 0	0.05	0.33	1.40	0.020	0.005	2.03	0.80		0.80	0.022	0.007	0.008	0.019	0.0028
Example Steel 3 0	0.05	0.30	1.40	0.020	0.004	2.00	09.0	0.20	0.80	0.021	0.01	0.02	0.020	0.0035
Comparative Example Steel 1 0.	0.05	0.32	1.39	0.020	0.004	2.00	,	,	00.0	0.021	,		0.020	0.0050
Comparative Example Steel 2 0.	0.05	0.30	1.38	0.020	0.005	2.00	0.81		0.81	0.019	,	1	0.021	0.0050
Comparative Example Steel 3 0.	0.05	0.30	1.40	0.019	0.004	2.01	09.0	0.19	0.79	0.021	-	-	0.019	0.0050
KA36 0.	0.10	0.34	1.42	0.017	0.002	0.02	,	ı	00.0	0.023	ı	t	r	0.0050

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Table 16

			40°C x 5 Cycles	ŋ		
		Corrosion Weight Loss	Loss	ŭ	Depth of Corrosion	
Type of Steel	Weight Loss (mg/cm²)	Average Decrease in Thickness (One Side, mm)	Ratio with Respect to Comparative Example RA36 (%)	Maximum Depth of Corrosion (mm)	Average Depth of Corrosion (mm)	Evaluation of Corrosive Surface
Example Stool 1	53	0.068	56	0.34	0.24	6
Comparative Example Steel 1	55	0.070	59	0.35	0.25	0
Example Steel 2	44	0.056	47	0.32	0.23	0
Comparative Example Steei 2	47	090.0	50	0.34	0.24	0
Example Steel 3	41	0.052	77	0.31	0.21	0
Comparative Example Steel 3	97	0.059	67	0.33	0.24	0
KA36	64	0.120	100	0.5	0.41	۵

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Table 17

	Base Metal	Simulated Heat Affected Zone (HAZ)
Type of Steel	Charpy Impact Energy	Charpy Impact Test
	Absorbed Energy vEo (J)	Absorbed Energy vEo (J)
fxample Steel 1	310	148
Example Steel 2	290	135
Example Steel 3	285	129
Comparative Example Steel 1	270	40
Comparative Example Steel 2	230	35
Comparative Example Steel 3	225	40
KA36	260	121

Table 18

	Ī .	T			T	
Remarks	Not included within the manufacturing conditions according to the present invention	Included within the manufacturing conditions according to the present invention	Not included within the manufacturing conditions according to the present invention	Included within the manufacturing conditions according to the present invention	Not included within the manufacturing conditions according to the present invention	Not included within the manufacturing conditions according to the present invention
Temperature at Which Cooling is Stopped (°C)	Ī.	200	650	200	350	500
Cooling Rate After Rolling (°C/sec)	0.5	5	15	15	15	25
Temperature at Which cooling Starts After Rolling (°C)	006	006	006	006	006	006
Manufacturing Condition	Ą	А	U	Q	ш .	β÷

Table 19

				40°C × 5 Cycles	1es			Absorbed	
Type of Steel	Manufacturing)	Corrosion Weight Loss	880	Jeg	Depth of Corrosion	ion	onergy vEo (Base	Remarks
	Conditions	Weight Loss (mg/cm ²)	Average Decrease in Thickness (One Side, mm)	Ratio with Respect to Comparative Example KA36	Maximum Depth of Corrosion (mm)	Average Depth of Corrosion (mm)	Evaluation of Corrosive Surface	Metal) (J)	
Example Steel 2	A	72	0.092	7.1	0.43	0.31	0		Comparative ex.
Example Steel 2	E	09	0.076	99	98.0	0.24	(O)		Example
Example Steel 2	ပ	68	0.087	7.2	0.42	0.29	0		Comparative ex.
Example Steel 2	D	56	0.071	09	0.34	0.26	© I O		Example
Example Steel 3	A	57	0.073	61	0.36	0.24	0		Comparative ex.
Example Steel 3	Q	48	0.061	51	0.34	0.23	0		Example
Example Steel 4	A	35	0.045	37	0.33	0.25	0	290	Comparative ex.
Example Steel 4	æ	33	0.042	35	0.27	0.20	0	302	Example
Example Steel 4	U	35	0.045	37	0.32	0.26	0	292	Comparative ex.
Example Steel 4	Ω	29	0.037	31	0.29	0.22	0	310	Example
Example Steel 4	ſĸὶ	29	0.037	31	0.29	0.23	0	220	Comparative ex.
Example Steel 4	De.	30	0.038	32	0.31	0.24	0	210	Comparative ex.
KA36	Ą	94	0.120	100	0.50	0.41	٧	260	Comparative ex.

 \otimes : a uniform corrosive condition with slightly uneven surface O: a uniform corrosive condition with a rather largely uneven surface Δ : a largely uneven surface with a small number of shallow pits

Table 20

				40°C × 5 Cycles	les			Absorbed	
Type of Steel	Manufacturing		Corrosion Weight Loss	880	Del	Depth of Corrosion	ion	Energy vEo (Base	Romarks
	Conditions	Weight Loss (mg/cm ²)	Average Decrease in Thickness (One Side, mm)	Ratio with Respect to Comparative Example KA36	Maximum Depth of Corrosion (mm)	Average Depth of Corrosion (mm)	Evaluation of Corrosive Surface	Metal) (J)	
Example Steel 7	А	31	0.039	37	0.30	0.27	0 1 0	266	Comparative ex.
Example Steel 7	В	27	0.034	33	0.27	0.26	0	285	Example
Example Steel 7	ວ	30	0.038	38	0.30	0.26	0 1 @	266	Comparative ex.
Example Steel 7	Q	26	0.033	28	0.28	0.25	0	290	Example
Example Steel 7	ਬ	26	0.033	28	0.28	0.26	0	212	Comparative ex.
Example Steel 7	P	27	0.034	29	0.29	0.27	0 	195	Comparative ex.
KA36	Ą	95	0.121	100	05.0	0.41	۵	260	Comparative ex.

©: a uniform corrosive condition with slightly uneven surface
O: a uniform corrosive condition with a rather largely uneven surface
A: a largely uneven surface with a small number of aboline also

a largely uneven surface with a small number of shallow pits

Table 21

	Renarks		Comparative ex.	Example	Comparative ex.	Example	Comparative ex.	Comparative ex.	Comparative ex.
Absorbed	Energy vEo (Base	Metal) (J)	270	275	272	278	220	202	260
	ston	Evaluation of Corrosive Surface	0	0	0	0 1 @	0 ®	0 1 @	۵
	Depth of Corrosion	Average Depth of Corrosion (mm)	0.30	0.28	0.31	0.27	0.27	0.28	0.41
		Maximum Depth of Corrosion (mm)	0.45	07.0	0.45	0.37	0.37	0.38	0.50
40°C × 5 Cycles	880	Ratio with Respect to Comparative Example KA36	32	30	32	29	29	30	100
	Corrosion Weight Loss	Average Decrease in Thickness (One Side, mm)	0.038	0.036	0.038	0.034	0.034	0.036	0.120
Weight Loss (mg/cm ²)			30	28	30	27	27	28	94
1	Manufacturing	Conditions	A	В	၁	Q	ធ	F	A
	Type of Steel		Example Steel 6	KA36					

©: a uniform corrosive condition with slightly uneven surface O: a uniform corrosive condition with a rather largely uneven surface Δ: a largely uneven surface with a small number of shallow pits

Table

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ex. Comparative ex. Comparative ex. Comparative ex. Comparative ex. Example Example Comparative Remarks Absorbed
Energy
vEo
(Base
Metal)
(J) 295 310 295 290 260 220 202 of Corrosive Surface Evaluation 0 0 0 0 0 ı ı 0 ٥ 0 0 Depth of Corrosion Average Depth of Corrosion 0.19 0.13 0.26 0.13 0.41 0.25 0.19 Maximum Depth of Corrosion (mm) 0.30 0.30 0.50 0.27 0.25 0.25 0.27 40°C x 5 Cycles Ratio with
Respect to
Comparative
Example KA36
(%) 100 29 28 24 22 22 23 Corrosion Weight Loss Average
Decrease in
Thickness
(One Side, mm) 0.028 0.120 0.034 0.029 0.033 0.027 0.027 Weight Loss (mg/cm²) 27 23 56 22 96 2.1 Manufacturing Conditions Ç ы Type of Steel Example Steel Example Steel Example Steel Example Steel Example Steel Example Steel KA36

©: a uniform corrosive condition with slightly uneven surface O: a uniform corrosive condition with a rather largely uneven surface

Δ: a largely uneven surface with a small number of shallow pits

Table 23

Type of Steel	U	Si	Мn	Ъ	S	A1	Cr	FN	γ	Ni+Mo	ИЪ	Ħ	кем	z
Example Steel 1	0.05	0.32	1.42	0.020	0.005	0.020 0.005 0.020	2.02	1	1	00.0	ı	0.01	0.008	0:0030
Example Steel 2	0.05	0.30	1.40	0.020	0.005	0.020 0.005 0.025	2.03	0.41	0.20	0.61	ı	0.02	0.010	0.0040
Example Steel 3	0.05	0.32	1.42	0.020	0.020 0.004 0.021	0.021	2.02	1	•	00.0	0.02	0.01	0.008	0.008 0.0030
Example Steel 4	0.05	08.0	1.40	0.020	0.004	0.004 0.021	2.00	09.0	0.20	08.0	0.02	0.02	0.010	0,0040

Table

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Evaluation of Corrosive Surface 0 0 0 0 0 0 0 0 ٥ Depth of Corrosion Average Depth of Corrosion (mm) 0.23 0.23 0.24 0.16 0.41 0.24 0.2 0.21 0.21 Maximum Depth of Corrosion (mm) 0.36 0.34 0.32 0.34 0.31 0.31 0.27 0.3 0.5 40°C x 5 Cycles Ratio with Respect to Comparative Example KA36 (1) 9 20 64 40 99 4.7 77 34 100 Corrosion Weight Loss Average Decrease in Thickness (One Side,mm) 090.0 0.059 0.048 0.068 0.056 0.052 0.041 0.120 0.071 Weight Loss (mg/cm²) 99 47 94 53 77 7 32 6 Manufacturing Conditions Ω A < Ω Ą Ω A Ω ď Type of Steel Example Steel KA36

 $\ensuremath{\text{@}}\colon$ a uniform corrosive condition with slightly uneven surface $\Delta\colon$ a largely uneven surface with a small number of shallow pits

Table 25

		Columnia	Nema I No	Comparative Example	Example	Comparative Example						
Simulated Heat Affected	Zone (HAZ)	Charpy Impact Test	Absorbed Energy VEO (J)	138	145	130	140	148	160	129	135	121
Base Metal		Charpy Impact Test	Absorbed Energy vEo (J)	299	310	282	300	310	320	285	295	260
		Manufacturino	Conditions	V	Q	Ą	Q	A	Q	A	D	A
		Type of Steel		Example Steel 1	Example Steel 1	Example Steel 2	Example Steel 2	Example Steel 3	Example Steel 3	Example Steel 4	Example Steel 4	KA36

Claims

1. A sea-water corrosion resistant steel suitable for use in a hot and wet environment comprising about: 0.1 wt% or less of C; 0.5 wt% or less of Si; 5 1.50 wt% or less of Mn; 0.005 to 0.050 wt% of AI; 0.5 to 3.50 wt% of Cr; and the balance Fe and incidental impurities. 10 A sea-water corrosion resistant steel according to claim 1 further comprising about: 1.5 wt% or less of Ni; and 0.8 wt% or less of Mo; and wherein the total quantity of Ni and/or Mo is 1.5 wt% or less. 15 A sea-water corrosion resistant steel according to claim 1 further comprising about: 0.005 to 0.05 wt% of Nb; and 0.005 to 0.05 wt% of Ti; such that the total quantity of Nb and/or Ti is 0.005 to 0.05 wt%. 20 A sea-water corrosion resistant steel according to claim 1 further comprising about: 1.5 wt% or less of Ni; 0.8 wt% or less of Mo such that total quantity of Ni and/or Mo is 1.5 wt% or less; 0.005 to 0.05 wt% of Nb; and 0.005 to 0.05 wt% of Ti such that total quantity of Nb and/or Ti is 0.005 to 0.05 wt%. 25 A sea-water corrosion resistant steel according to claim 1 further comprising about: 0.0015 to 0.020 wt% of REM; 0.005 to 0.05 wt% of Ti; and 0.0020 to 0.0120 wt% of N. 30 A sea-water corrosion resistant steel according to claim 2 further comprising about: 0.0015 to 0.020 wt% of REM; 0.005 to 0.05 wt% of Ti: and 0.0020 to 0.0120 wt% of N. 35 A sea-water corrosion resistant steel according to claim 1 further comprising about: 0.005 to 0.05 wt% of Nb; 0.005 to 0.05 wt% of Ti such that total quantity of Nb and Ti is 0.005 to 0.05 wt%; 0.0015 wt% to 0.020 wt% of REM; and 0.0020 to 0.0120 wt% of N. 40 A sea-water corrosion resistant steel according to claim 1 further comprising about: 0.005 to 0.05 wt% of Nb; 0.005 to 0.05 wt% of Ti; such that total quantity of Nb and Ti is about 0.005 to 0.05 wt%; 45 1.5 wt% or less of Ni; 0.8 wt% or less of Mo; such that total quantity of Ni and/or Mo is about 1.5 wt%;

0.0015 to 0.020 wt% of REM; and 0.0020 to 0.0120 wt% of N.

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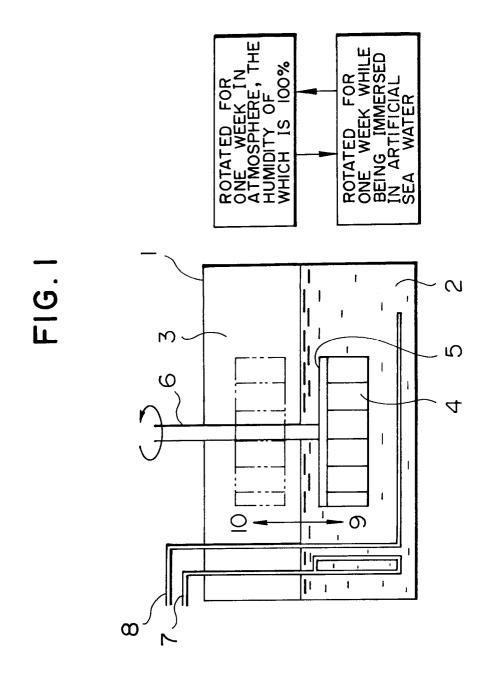
9. A method of manufacturing sea-water corrosion resistant steel suitable for use in a hot and wet environment comprising the steps of:

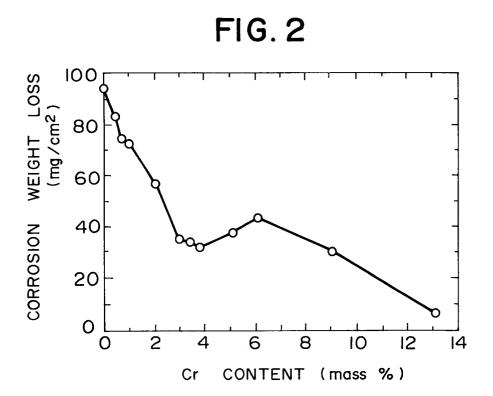
casting and hot-rolling steel comprising about 0.1 wt% or less of C, 0.5 wt% or less of Si, 1.50 wt% or less of Mn, 0.005 to 0.050 wt% of Al, 0.5 to 3.50 wt% of Cr, and the balance Fe and incidental impurities; accelerated cooling said steel at a cooling rate of about 3 to 20°C/sec immediately after said steel has been heated due to casting and hot rolling;

stopping said cooling when said steel has been cooled to about 400°C to 600°C; and

cooling said steel with air.

	10.	A method as	claimed in clain	n 9 wherein the	steel has a compo	osition as claimed in	any of claims 2 to 8.
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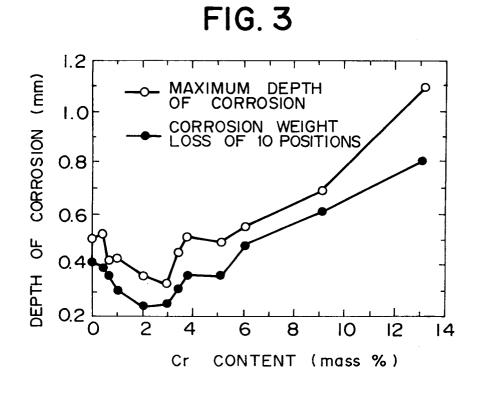


FIG.4A

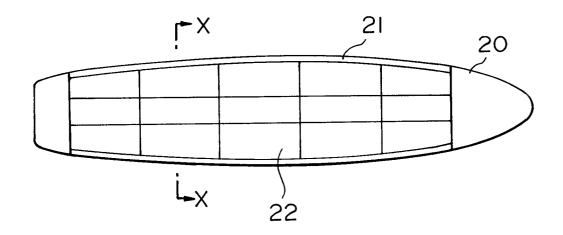
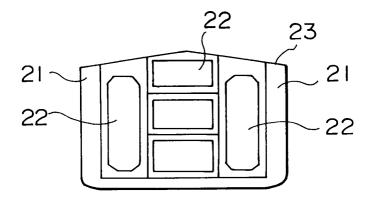


FIG. 4B





EUROPEAN SEARCH REPORT

Application Number EP 94 30 5057

ategory	Citation of document with income of relevant pas		Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.CL6)
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				TECHNICAL FIELDS SEARCHED (Int.Cl.6)
				C22C
	The present search report has b	een drawn up for all claims		
	Place of search	Date of completion of the search		Excerniner
	THE HAGUE	21 October 1994	<u> </u>	ppens, M
Y:pa	CATEGORY OF CITED DOCUME articularly relevant if taken alone articularly relevant if combined with an accument of the same category chnological background	E : earlier palent after the fills other D : document cit L : document cit	ed in the applicati ed for other reason	blished on, or on