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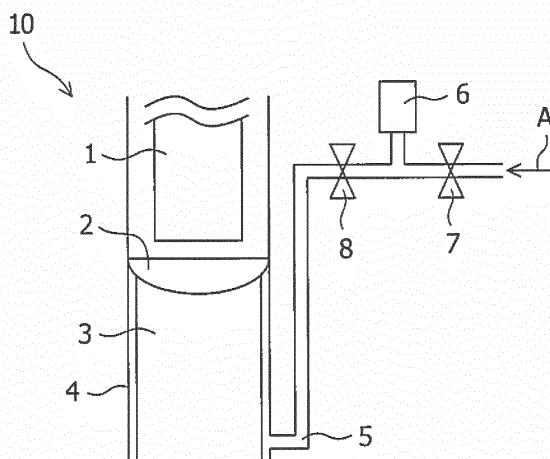
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(54) **PROCESS FOR MANUFACTURING MARAGING STEEL AND METHOD FOR REFINING INCLUSIONS**

(57) Provided is a method of producing maraging steel and a method of making Ti-based inclusions finer and making the sizes of Ti-based inclusions that may differ at different locations in the steel ingot more uniform. A method of producing a maraging steel by using vacuum arc remelting that uses a vacuum arc remelting apparatus

at least includes a steel ingot production step of producing a steel ingot by melting a consumable electrode made of maraging steel in a crucible of the apparatus, and in this method, the steel ingot production step includes cooling the steel ingot with rare gas introduced between the steel ingot and the crucible.

FIG.1



Description

TECHNICAL FIELD

5 **[0001]** The present invention relates to a method of producing maraging steel and a method of making inclusions finer in maraging steel.

BACKGROUND ART

10 **[0002]** Maraging steel has a very high tensile strength of around 2,000 MPa, and is thus used for a variety of purposes including parts that require a high strength, such as metal crucibles and parts for rockets, centrifugal separators, aircrafts, and continuously variable transmissions for automotive engines.

[0003] Maraging steel usually contains proper amounts of Mo and Ti as strengthening elements, and can realize high strength by causing intermetallic compounds such as Ni_3Mo , Ni_3Ti , and Fe_2Mo to precipitate with aging treatment. A
15 typical composition of maraging steels containing Mo and Ti as described above includes, by mass percentage, 18%Ni-8%Co-5%Mo-0.45%Ti-0.1%Al.bal.Fe.

[0004] However, while maraging steel has very high tensile strength, its fatigue strength is not necessarily high. Non-metallic inclusions containing nitrides and carbonitrides such as TiN and TiCN (the non-metallic inclusions may be hereafter be simply referred to as "inclusions") have been considered as the main cause of degrading the fatigue strength.
20 In particular, TiN is present often in the shape of cuboid having sharp corner portions. The sharp corner portions of the cuboid shape may become a starting point of propagation of cracks into the metal base (matrix). As cracks propagate, the metal material may break. If the inclusions have small sizes, they may hardly become a starting point of fatigue breaking of metal materials. However, if such inclusions grow large in a metal material, fatigue breaking may occur with such inclusions as starting points.

25 **[0005]** In order to reduce the amount of the inclusions described above, vacuum arc remelting (hereinafter may also be referred to as "VAR") has been used. Maraging steel produced by applying VAR has the advantage that the components of the steel are distributed evenly, and also that the amount of inclusions becomes smaller.

[0006] However, even in maraging steels produced by using an apparatus for vacuum arc remelting, relatively large inclusions containing nitrides and carbonitrides such as TiN and TiCN remain as residues, and the residual large inclusions
30 will remain as they are in the material that has undergone hot forging, heat treatments, hot rolling, and cold rolling carried out after the VAR. Such residual large inclusions have been a cause of fatigue breaking that may occur due to the inclusions acting as starting points.

[0007] Focusing on the above-described problem caused by inclusions, proposals have been made to refine inclusions. For example, JP 2001-214212 A (Patent Document 1) proposes a method of producing Ti-containing steel, in which a
35 stock for Ti-containing steel that does not include TiN-based inclusions is melted in a vacuum induction furnace and casted into an electrode, and VAR is carried out by using the Ti-containing steel electrode, and the TiN-based inclusions are thereby made finer.

[0008] In addition, a method for refining, or making finer, Ti-based inclusions such as TiN and TiCN has been proposed. For example, JP 4692282 B1 (Patent Document 2) discusses a method of producing a steel ingot comprising an Mg
40 oxide formation step in which Mg is added to molten metal during primary vacuum melting for adjusting the composition of oxides mixed in the molten steel so as to make MgO a primary component, a step of obtaining a consumable electrode in which the Mg oxide remains by solidifying the molten steel after the Mg oxide forming step, and a dissociation step of remelting the consumable electrode with the atmospheric pressure being reduced compared with that in the Mg oxide forming step so as to dissociate the Mg oxide in the molten metal into Mg and oxygen and reduce the content of Mg to
45 be as low as 50% or lower of that in the Mg oxide forming step.

CITATION LIST

[Patent Documents]

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[0009]

[Patent Document 1] JP 2001-214212 A

[Patent Document 2] JP 4692282 B1

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SUMMARY OF INVENTION

Technical Problem

[0010] The method proposed by Patent Document 1 is characteristic in that Ti-based inclusions can be made finer by using a Ti-containing steel ingredient that does not contain Ti-based inclusions such as TiN and TiCN. To manage the quality of the ingredient itself is one way of reducing the amount of Ti-based inclusions, however, in this way, the costs may become problematically high because high-quality ingredients are necessarily expensive. Ti-based inclusions occur depending on melting conditions and the like. Accordingly, Ti-based inclusions may possibly grow large during the production process in accordance with melting conditions and the like. Therefore, managing ingredients may not solve problems.

[0011] On the contrary, the method of refining inclusions as discussed in Patent Document 2 utilizes Mg, and this method is very effective because Ti-based inclusions may become dramatically finer. If Ti-based inclusions that have been refined by the method discussed in Patent Document 2 can be further refined or if Ti-based inclusions having various sizes that differ depending on different locations within the steel ingot, after having gone through remelting, can be made more uniform, the quality and characteristics of maraging steel products may be further stabilized.

[0012] The purpose of the present invention is to provide a method of producing maraging steel and making inclusions finer which is capable of making Ti-based inclusions further finer and making more uniform the sizes of Ti-based inclusions that may differ depending on locations within the steel ingot.

Summary of the Invention

[0013] The inventors of the present invention have examined methods for making Ti-based inclusions in maraging steels further finer. As a result, the inventors have found that Ti-based inclusions can be made further finer, and the sizes of Ti-based inclusions different for different locations within the steel ingot can be made more uniform by using a method based on the vacuum arc remelting in which, while a steel ingot is produced by melting a consumable electrode made of maraging steel containing magnesium oxides, gas with high thermal conductivity is introduced between the steel ingot and crucible to cool the steel ingot so as to improve the efficiency of cooling the steel ingot, and has thus arrived at the present invention.

[0014] Specifically, according to an aspect of the present invention, a method of producing a maraging steel by using vacuum arc remelting and a vacuum arc remelting apparatus, comprising at least a steel ingot production step of producing a steel ingot by melting a consumable electrode made of a maraging steel containing magnesium oxide in a crucible of the apparatus, wherein the steel ingot production step includes a cooling step of cooling the steel ingot with rare gas introduced between the steel ingot and crucible.

[0015] According to another aspect of the present invention, a method of refining inclusions in a maraging steel using vacuum arc remelting and a vacuum arc remelting apparatus, comprising at least a steel ingot production step of producing a steel ingot by melting a consumable electrode made of a maraging steel containing magnesium oxide in a crucible of the apparatus, wherein the steel ingot production step includes a cooling step of cooling the steel ingot with rare gas introduced between the steel ingot and crucible.

Advantageous Effects of the Invention

[0016] According to the present invention, Ti-based inclusions remaining in maraging steels can be refined and the size of the inclusions can be made uniform. As a result, fatigue breaking that may occur due to Ti-based inclusions as starting points can be suppressed.

BRIEF DESCRIPTION OF DRAWINGS

[0017] FIG. 1 is a schematic diagram which illustrates an example of a structure of a vacuum arc remelting apparatus that introduces rare gas according to the present invention.

DETAILED DESCRIPTION OF THE INVENTION

[0018] An embodiment of the present invention will be described below. However, the present invention is not limited by the embodiment described below in any respects.

[0019] The most important characteristic of the maraging steel production method of the present invention is to introduce rare gas between the crucible and the steel ingot that are going through VAR in the remelting process.

[0020] In maraging steel containing Ti, Ti-based inclusions occurring in the steel have a high-melting point, and thus

a part of the inclusions remains as residues during the remelting of a consumable electrode and is present as solid in the molten steel pool. The part of the inclusions grows when the molten steel pool is solidified and the steel ingot is produced. If the rate of cooling the steel ingot can be increased, the time for growth of Ti-based inclusions can be shortened as the inside of the steel ingot solidifies quickly, and it is thereby possible to refine, or make finer, the Ti-based inclusions. However, during VAR, even if the rate of melting the consumable electrode is varied, it is difficult to greatly vary the rate of cooling during solidification for the same diameter of the steel ingot. This is because during VAR, a gap is created between the steel ingot and the water-cooled copper crucible when the steel ingot solidifies and contracts, and conductive heat transfer becomes cut off due to the gap. Another reason is that according to the conventional art, convective heat transfer hardly occurs because the above-described gap is under reduced pressure atmosphere, thus the heat is primarily released by radiative heat transfer only, and thereby cooling of the steel ingot does not appropriately progress. According to conventional art, because the rate of release of heat from the steel ingot is limited to the heat transfer between the steel ingot and the crucible, the rate of cooling of steel ingot during VAR is greatly dependent on the diameter of the steel ingot.

[0021] Accordingly, the production method according to the present invention includes a cooling process in which, when a steel ingot is produced, rare gas is introduced into the gap between the steel ingot and the crucible by using a gas introduction nozzle, such as a rare gas introduction pipe, to cool the steel ingot, so as to release heat from the steel ingot by the convective heat transfer between the steel ingot and the crucible, and thereby increase the rate of cooling of the steel ingot which is being solidified. As a result, the growth of Ti-based inclusions is controlled during VAR and thus Ti-based inclusions are made finer. Further, because it is possible to increase the rate of cooling of the entire steel ingot by introducing rare gas starting from the initial stage of melting by VAR, coarsening of the Ti-based inclusions in the longitudinal and radial directions of the steel ingot can be prevented, and the size of the Ti-based inclusions that may differ according to different locations in the steel ingot can be made more uniform.

[0022] According to the present invention, as described above, rare gas is introduced into the gap between the steel ingot and the crucible. Because rare gas does not chemically react with the molten steel or the steel ingot, no inclusions would be newly generated. Further, the risk of explosion that may occur due to chemical reactions can be prevented using rare gas. Considering the rate of cooling of the steel ingot, it is preferable to use a rare gas with a high thermal conductivity among various types of rare gases, and He is the most preferable because it has the highest thermal conductivity among them. Also, a helium gas which contains impurity gases in amounts with which the chance of chemical reactions with the molten steel and the steel ingot may be ignored should be used. In order to secure the cooling effect of such He gas, the purity of He is preferable to be 99.9 vol. % or higher.

[0023] FIG. 1 is a schematic diagram which illustrates an example of the structure of the vacuum arc remelting apparatus that introduces rare gas according to the present invention. Using this drawing, described is the cooling process which includes introduction of rare gas into the crucible in the vacuum arc remelting apparatus via a rare gas introduction pipe. Referring to Fig. 1, when the operation of a vacuum arc remelting apparatus 10 is started, a consumable electrode 1 for remelting melts and drops to form a molten steel pool 2, and a steel ingot 3 is formed. A water-cooled copper crucible 4 cools the steel ingot 3. Rare gas A is introduced between the steel ingot 3 and the water-cooled copper crucible 4 from a rare gas cylinder (not illustrated) via a gas introduction nozzle 5 to cool the steel ingot 3. The introduction pressure for the rare gas A is controlled by measuring the pressure inside the gas introduction nozzle 5 for feeding the gas from the rare gas cylinder to the water-cooled copper crucible 4 with a pressure measuring device 6, and by providing a pressure control valve 7.

[0024] By increasing the pressure of the rare gas, the heat capacity per unit volume of the gas is increased, and the effect of the convective heat transfer can be increased. From the above-described viewpoints, if the pressure inside the gas pipe is below 100 Pa, the effect of the convective heat transfer is low, and accordingly, the effect of increasing the rate of cooling becomes low. In addition, because the vacuum arc remelting apparatus operates always under reduced-pressure atmosphere, even if the pressure of the rare gas introduced into the gap between the steel ingot and the crucible is increased, the rare gas may escape from a contacting portion between the steel ingot and the crucible, and the rare gas may be exhausted by the vacuum pump. If the rare gas for cooling the steel ingot escapes from the contacting portion between the steel ingot and the crucible, the escaped rare gas may enter into a region between the melting electrode and the molten steel pool. In this case, the arcing may become unstable due to the entering rare gas, and inclusions may increase. Further, even if the pressure of the rare gas is excessively increased, it also becomes difficult to increase the effect of the convective heat transfer. In order to promote denitration and evaporation of Mg from the molten steel, it is preferable to control the pressure of the reduced-pressure atmosphere as low as possible. Accordingly, it is not preferable to introduce an excessive amount of rare gas because the denitration and the evaporation of Mg are hindered. Considering the above-described reasons, it is preferable to set the pressure inside the pipe for introducing the rare gas in a range of 100 Pa to 3,000 Pa. A lower limit of the pressure inside the pipe for introducing the rare gas is preferably 100 Pa, more preferably 600 Pa, and yet more preferably 1,000 Pa. If the pressure is 1,000 Pa or higher, the effect of reducing the depth of the molten steel pool becomes remarkable. It is particularly preferable to control the pressure in this range, because in this pressure range, the solid-liquid coexistence region in which TiN crystallizes and

grows becomes small, and it is possible to secure the effect of refining TiN. An upper limit of the pressure inside the pipe for introducing He gas is preferably 3,000 Pa, more preferably 2,500 Pa, and yet more preferably 1,900 Pa. This is because the rate of cooling is increased by increasing the pressure of He gas, however, if the pressure of He gas is excessively increased, the gas is evacuated and may not contribute to the cooling, decreasing its effectiveness.

[0025] The maraging steel production method is particularly effective for steel ingots with an average diameter of 300 mm to 800 mm. This is because as the diameter of a steel ingot becomes larger, the influence from the thermal resistance of the steel ingot itself becomes greater due to an influence from the convective heat transfer between the steel ingot and the crucible and because the rate of cooling of the steel ingot is dependent on the diameter of the steel ingot. If the thermal conductivity of the steel ingot becomes lower, the rate of cooling of the steel ingot tends to depend more on the diameter of the steel ingot, and the effect of increasing the rate of cooling of a steel ingot becomes remarkable for the average steel ingot diameter of 300 mm or larger. If the average diameter of the steel ingot is less than 300 mm, the rate of cooling is sufficiently high even if rare gas is not introduced, and therefore, the effect of increasing the rate of cooling becomes low even if rare gas is introduced. On the other hand, if the average diameter of the steel ingot is larger than 800 mm, even if the effect of the convective heat transfer between the steel ingot and the crucible is increased by introducing rare gas, the release of heat may be inhibited due to the heat resistance of the steel ingot itself, and thus the effect of increasing the rate of cooling even to the center of the steel ingot may become low in some cases. Accordingly, it is preferable to set the average diameter of the steel ingot between 300 mm and 800 mm.

[0026] Note that in producing maraging steel, the diameter of the steel ingot is not constant and is slightly uneven for the entire ingot. Accordingly, in determining the diameter of the steel ingot, an average diameter of the steel ingot is calculated and used.

[0027] The rate of cooling of the steel ingot can be set within a range from 0.01°C/sec to 0.1°C/sec. The rate of cooling of the steel ingot means the rate of cooling at the center portion of the steel ingot. It is difficult to determine measurement values of the cooling rate during actual operations. Therefore, it is preferable, for example, to determine the rate of cooling by carrying out simulations prior to melting.

[0028] Note that in order to secure the above-described effect of increasing the rate of cooling the steel ingot by introducing rare gas, it is effective, for example, to provide a plurality of inlet for the rare gas to be introduced during the steel ingot production process so that fresh rare gas can be always introduced into the solidification region of the steel ingot.

[0029] In the maraging steel production method of the present invention, the consumable electrode is maraging steel containing magnesium oxides. This consumable electrode is melted inside the crucible of the vacuum arc remelting apparatus to produce a steel ingot (the steel ingot production process). Ti-based inclusions easily crystallize in the form of Ti-based inclusion-MgO complexes that contain oxides made up mostly of magnesium oxide (MgO) as their cores. Therefore, the maraging steel has finely dispersed Ti-based inclusions as it contains magnesium oxides. Thus, if a consumable electrode made of maraging steel containing magnesium oxides is manufactured utilizing the cooling process during the manufacture of steel ingots, Ti-based inclusions remaining in the maraging steel can be made finer and the size of the inclusions can be made uniform.

[0030] According to the present invention, the growth of Ti-based inclusions is prevented during the steel ingot production process. The consumable electrode made of the maraging steel containing magnesium oxides used in this process can be produced, for example, by adding magnesium to the maraging steel and vacuum melting the steel (the consumable electrode production process).

[0031] In this consumable electrode production process, the consumable electrode for remelting of maraging steel having Mg oxides is obtained. This is because if this process is carried out, it becomes easy for Ti-based inclusions to crystallize with the oxides mostly made up of MgO as cores, and thus Ti-based inclusions can be transformed into complexes of Ti-based inclusion and MgO. Further, the Ti-based inclusions can be present dispersed in the consumable electrode.

[0032] In order to transform the oxides contained in the consumable electrode into oxides mostly made up of Mg oxide, it is preferable to have add an amount of Mg in the consumable electrode production process in a range from 10 ppm to 200 ppm.

[0033] In performing VAR using the consumable electrode, the atmospheric pressure should be reduced as much as possible by adjusting the strength of vacuum pumping so that the evaporation of Mg from the surface of the molten steel during remelting is promoted. After Mg has evaporated, the MgO portion that constitutes part of the Ti-based inclusion-MgO complexes is eliminated. Thus, the residual Ti-based inclusions remain finely dispersed, and it becomes possible to melt the the Ti-based inclusions completely in the molten steel thanks to promoted thermal decomposition. That is, if the Ti-based inclusions are completely melted once during VAR, the size of the Ti-based inclusions become dependent on their growth during solidification in VAR. Accordingly, the above-described effect of introducing the rare gas can be excellently exhibited.

[0034] The maraging steel production method of the present invention is effective for making Ti-based inclusions finer as described above. Accordingly, the present invention is particularly effective in producing the maraging steel to which Ti is positively added. Preferable compositions are as follows. Note that units are in % by mass.

[0035] Titenium (Ti) forms a fine intermetallic compound when subjected to aging treatment and is an essential element that contributes to the strength of steel by precipitation. It is preferable to have Ti at 0.2% or more. However, if the content of Ti to be added exceeds 3.0%, the ductility and toughness may degrade. Accordingly, it is preferable to have 3.0% or less of Ti.

[0036] Oxgene (O) is an element that forms oxide-based inclusions. It is preferable to reduce the amount of oxygen that forms oxide-based inclusions. Accordingly, it is preferable to limit the O content to less than 0.001 %.

[0037] Nitrogen (N) is an element that forms nitride inclusions and carbonitride inclusions. The present invention is capable of refining nitride-based inclusions, but it is preferable to reduce the amount of nitrogen that forms the nitride-based inclusions. Accordingly, it is preferable to limit the N content to a level below 0.0015%.

[0038] Carbon (C) forms carbides and carbonitrides and causes the fatigue strength to degrade by reducing the amount of precipitated intermetallic compounds, and thus it is preferable to have an upper limit of the content of C at 0.01% or less.

[0039] Nickel (Ni) is an essential element for forming a mother phase structure with high toughness. If its content is 8% or less, the toughness degrades. On the other hand, if its content exceeds 22%, the austenite becomes stable and it becomes difficult to form a martensite structure. Therefore, it is preferable to have 8 to 22% of Ni.

[0040] Cobalt (Co) is an element that contributes to precipitation and strength by reducing the solid solubility of Mo so as to promote precipitation of Mo and form fine intermetallic compounds without greatly affecting the stability of the martensitic structure that is the matrix. However, if its content is less than 5%, the effect may not be satisfactory, while if its content exceeds 20%, brittleness tends to develop. Therefore, it is preferable to have 5 to 20% of Co.

[0041] Molybdenum (Mo) is an element that forms fine intermetallic compounds when subjected to aging treatment and contributes to strength by precipitation in the matrix. However, if its content is less than 2%, such effect may be limited, while if its content exceeds 9%, coarse deposits that degrade ductility and toughness tend to form. Therefore, it is preferable to have 2 to 9% of Mo.

[0042] Aluminum (Al) not only contributes to strength by age precipitation but also has a deoxidation action, and it is preferable to have 0.01% or more of Al, while if the content of Al exceeds 1.7%, toughness degrades. Therefore, it is preferable to have 1.7% or less of Al.

[0043] Other than those described above, the balance can be Fe. Because boron (B) is an element effective for refining of crystal grains, B may be added in a range of 0.01% or less since the toughness is not degraded in this range of B content. Inevitable impurity elements may be present in certain cases.

[0044] Next, the method of making inclusions finer in maraging steel according to the present invention will be described. The refining is achieved by vacuum arc remelting in a vacuum arc remelting apparatus. The method at least includes the steel ingot production process of producing a steel ingot by melting a consumable electrode made of maraging steel containing magnesium oxides in the crucible of the apparatus.

[0045] Ti-based inclusions easily crystallize in the form of Ti-based inclusion-MgO complexes containing oxides mostly made up of magnesium oxide (MgO) as their cores. The maraging steel containing magnesium oxides has finely dispersed Ti-based inclusions. Accordingly, if a consumable electrode made of maraging steel containing magnesium oxides is used, by performing the production method which includes the steel ingot production process containing a cooling process, Ti-based inclusions remaining in the maraging steel can be made finer and their size can be made more uniform.

[0046] This steel ingot production process includes the cooling of the steel ingot using rare gas introduced between the steel ingot and the crucible. This is because it becomes possible to increase the rate of cooling the solidified steel ingot by convective heat transfer between the steel ingot and the crucible. As a result, it becomes possible to prevent Ti-based inclusions from growing during VAR and make the Ti-based inclusions finer. Further, because it becomes possible to increase the rate of cooling of the entire steel ingot by introducing the rare gas starting from the initial stage of melting by VAR, coarsening of the Ti-based inclusions in the longitudinal and radial directions of the steel ingot can be prevented, and the size of the Ti-based inclusions that may differ at different locations of the steel ingot can be made more uniform.

[0047] The rate of cooling the steel ingot can be set within a range from 0.01°C/sec to 0.1°C/sec. The rate of cooling the steel ingot means the rate of cooling at the center portion of the steel ingot.

[0048] In the present invention, rare gas is introduced into the gap between the steel ingot and the crucible. Because rare gas does not chemically react with molten steel or the steel ingot, no inclusions would be newly formed, and considering the rate of cooling the steel ingot, it is preferable to use a rare gas with a high thermal conductivity among various types of rare gases, and helium (He) is the most preferable because it has the highest thermal conductivity among rare gases. The risk of explosion due to chemical reactions can be avoided using rare gas. In addition, if He is used, He gas that contains impurity gases in amounts with which the degree of chemical reaction between the molten steel and the steel ingot can be ignored should be used. In order to obtain a sufficient cooling effect, the purity of He should be 99.9 vol.% or higher.

[0049] The cooling process can include a rare gas introduction process of introducing rare gas into the crucible via a rare gas introduction pipe. By increasing the pressure of the rare gas, the heat capacity per unit volume of the gas is increased, so that the convective heat transfer increases. If the pressure inside the gas pipe is below 100 Pa, the effect

of the convective heat transfer is low, and accordingly, the rate of cooling becomes low. In addition, because the vacuum arc remelting apparatus operates always under reduced-pressure atmosphere, even if the pressure of the rare gas that has been introduced into the gap between the steel ingot and the crucible is increased, the rare gas may be exhausted by the vacuum pump. Therefore, even if the pressure of the rare gas is increased to exceed 3,000 Pa, it becomes difficult to increase the effect of convective heat transfer. Further, in order to promote denitration and evaporation of Mg from the molten steel, it is preferable to control the pressure of the reduced-pressure atmosphere as low as possible. Accordingly, it is not useful to introduce excessive amounts of the rare gas because the denitration and the evaporation of Mg are hindered. Accordingly, it is preferable to set the pressure inside the pipe for introducing the rare gas in a range of 100 Pa to 3,000 Pa. A lower limit of the pressure inside the pipe for introducing the rare gas is preferably 100 Pa, more preferably 600 Pa, and yet more preferably 1,000 Pa. An upper limit of the pressure inside the pipe for introducing He gas is preferably 3,000 Pa, more preferably 2,500 Pa, and yet more preferably 1,900 Pa.

[0050] The method of refining inclusions in a maraging steel is particularly effective for a steel ingot with an average diameter of 300 mm to 800 mm. This is because as the diameter of a steel ingot becomes larger, the influence from the thermal resistance of the steel ingot itself becomes greater than the effect of the convective heat transfer between the steel ingot and the crucible and because the rate of cooling of the steel ingot becomes more dependent on the diameter of the steel ingot. If the thermal conductivity of the steel ingot itself becomes lower, the rate of cooling of the steel ingot tends to depend on the diameter of the steel ingot, and the effect of increasing the rate of cooling a steel ingot becomes remarkable for the average steel ingot diameter of 300 mm or larger. If the average diameter of the steel ingot is less than 300 mm, the rate of cooling is sufficiently high even if the rare gas is not introduced, and therefore, the effect on increasing the rate of cooling by the introduced rare gas becomes low. On the other hand, if the average diameter of the steel ingot is larger than 800 mm, even if the effect of the convective heat transfer between the steel ingot and the crucible is increased by introducing the rare gas, the heat release is inhibited due to the heat resistance of the steel ingot itself, and thus the effect of increasing the rate of cooling even to the center of the steel ingot may become low in some cases. Accordingly, it is preferable to have the average diameter of the steel ingot at 300 mm to 800 mm.

[0051] Note that in the method of refining inclusions in maraging steel, the diameter of the steel ingot is not constant and is slightly uneven for the entire ingot. Accordingly, in determining the diameter of the steel ingot, an average diameter of the steel ingot is calculated and used.

[0052] The growth of Ti-based inclusions is prevented by the steel ingot production process of the present invention. The consumable electrode made of maraging steel containing magnesium oxides used in this process can be produced by adding magnesium to maraging steel prior to vacuum melting, for example (the consumable electrode production process).

[0053] According to this consumable electrode production process, consumable electrodes for remelting of maraging steel having Mg oxides is obtained. It becomes easy for Ti-based inclusions to crystallize with oxides mostly made up of MgO as their cores, and thus Ti-based inclusions can be transformed into complexes of Ti-based inclusions and MgO. Further, the consumable electrodes have dispersed Ti-based inclusions.

[0054] In order to transform the oxides contained in the consumable electrode into oxides mostly made up of Mg oxide, it is preferable to add 10 ppm to 200 ppm of Mg.

[0055] In performing VAR using the consumable electrode, the atmosphere should be controlled to have a pressure as low as possible, so that the evaporation of Mg from the surface of the molten steel during remelting is promoted. After Mg has evaporated, the MgO portion that constitutes part of the Ti-based inclusion-MgO complexes is eliminated. The residual Ti-based inclusions are finely dispersed, and it becomes possible to completely melt the Ti-based inclusions in the molten steel due to promoted thermal decomposition. Because Ti-based inclusions are completely melted by performing VAR, the size of the Ti-based inclusions then become dependent on their growth during solidification in VAR. Accordingly, the above-described effect of introducing the rare gas can be excellently exhibited.

EXAMPLES

[0056] Hereinbelow, the present invention will be more specifically described with reference to Examples and Reference Examples, however, the present invention is not limited by the following examples in any respects.

(Aspect 1)

[0057] The present invention will be described in detail with reference to Aspect 1. For the consumable electrode production process, a consumable electrode for vacuum arc remelting was produced by vacuum melting. In producing the consumable electrode, 14 ppm of Mg was added to form Mg oxide. A test piece was sampled from the consumable electrode, the test piece was dissolved in a nitric acid solution, and the solution was filtered through a 5 μ m filter to obtain inclusions from the consumable electrode as a residue insoluble in nitric acid. The obtained inclusions were observed using a scanning electron microscope (SEM), and energy dispersive X-ray spectroscopy (EDS) was performed

to verify the presence or absence of Mg oxide. As a result, it was verified that the inclusions were TiN-based containing MgO as cores. The consumable electrode was remelted by VAR to produce a steel ingot.

[0058] Note that in order to realize the same composition of the electrode for remelting, the same number and size of the inclusions for both the Examples and the Reference Examples, during the consumable electrode production process, molten steel was molded simultaneously using molds having the same shape, to produce two electrodes for remelting. Vacuum arc remelting was carried out by using the vacuum arc remelting apparatus 10 shown in FIG. 1. In an example of the present invention, when one of the two electrodes 1 for remelting was remelted by VAR, He gas of 4 N or higher according to the industrial He gas purity specification, i.e., He gas with 99.99% purity or higher, was introduced between the steel ingot 3 and the water-cooled copper crucible 4, and this example is referred to as "Example No. 1". When the other electrode for remelting was remelted by vacuum arc remelting, He gas was not introduced between the steel ingot 3 and the water-cooled copper crucible 4, and this case is referred to as "Reference Example No. 11". In both the example of the present invention and the reference example, the average diameter of the steel ingot was 500 mm.

[0059] For cooling with the He gas, the electrode 1 for remelting was installed by using the vacuum arc remelting furnace illustrated in FIG. 1 and the melting was performed inside the water-cooled copper crucible 4. During the melting, the He gas was introduced into the gap between the steel ingot 3 and the water-cooled copper crucible 4 via the gas introduction nozzle 5 installed in a lower portion of the water-cooled copper crucible 4. The pressure inside the pipe for feeding the gas from the He gas cylinder to the crucible 4 was measured by using the pressure measuring device 6, and the pressure of the He gas was controlled to be always constant using the pressure control valve 7. The introduced He gas loaded into the gap between the steel ingot 3 and the water-cooled copper crucible 4 removed heat from the steel ingot 3, and escaped from the gap was finally exhausted to the outside by using a vacuum pump not illustrated in the drawing.

[0060] After a piping valve 8 installed to the pipe was opened during melting and it was verified that the pressure of the He gas was controlled at the set level, the melting of the electrode for remelting was continued. The pressure of the He gas inside the pipe used in Example No. 1 was 1,200 Pa. After the melting of the electrode was completed, the piping valve 8 installed to the pipe was closed, and further, the setting value for the pressure control apparatus was set to 0 Pa. The compositions of the electrodes for remelting used in the Example No. 1 of the present invention and the Reference Example No. 11, and the compositions of the steel ingot produced by the Example No. 1 of the present invention and the Reference Example No. 11 are shown in Table 1.

[Table 1]

No.		C	Ni	Mo	Co	Al	Ti	[Mg]	[N]	[O]
1	Electrode	0.0050	18.27	5.01	8.23	0.12	0.47	14	12	11
	Ingot	0.0053	18.27	5.01	8.23	0.12	0.47	2	7	4
11	Electrode	0.0050	18.27	5.01	8.23	0.12	0.47	14	12	11
	Ingot	0.0052	18.27	5.01	8.23	0.12	0.47	3	7	4

(% by mass)

The elements other than those shown above are Fe and inevitable impurities. The units of the content of the elements shown in parentheses are ppm.

[0061] Next, in order to sample test pieces for determining inclusions from the top portion, the intermediate portion, and the bottom portion of the steel ingot of the maraging steel remelted by VAR, the steel ingot was sectioned in the direction normal to the central axis at equal intervals, and test pieces of 2 g a piece for analyzing inclusions were sampled from the center portion of the steel ingot (D/2 portion, D = diameter of the steel ingot) and the intermediate radial portion (D/4 portion) of the top, intermediate, and bottom portions. The test pieces for inclusions analysis were dissolved in a nitric acid solution, and Ti-based inclusions insoluble in nitric acid, such as TiN and TiCN, were filtered through a filter. The residue remaining on the filter after the filtration was observed with SEM to determine the size of Ti-based inclusions containing TiN and TiCN.

[0062] Note that for the diameters of the Ti-based inclusions containing TiN and TiCN, the Ti-based inclusions were selected by SEM observation and the selected inclusions were photographed, the taken SEM photographs of the Ti-based inclusions were captured by image analysis software, the contours of the Ti-based inclusions were determined, areas of the inside of respective contours were calculated by image processing, and the respective areas were converted into circular areas, and the diameters of the circles were used as the diameters of the Ti-based inclusions. The largest among the diameters of all the Ti-based inclusions observed on the filter was used as the maximum length. The sizes of the Ti-based inclusions containing TiN and TiCN verified for the top, intermediate, and bottom portions are shown in Tables 2 and 3. Table 2 shows the results for the samples obtained from the center portion of the steel ingot (D/2 portion) and Table 3 shows the results for the samples obtained from the intermediate portion (D/4 portion of the radius of the steel ingot).

[Table 2]

No.	Maximum length of Ti-based inclusions (μm)			Description
	Top	Intermediate	Bottom	
1	7.19	7.10	7.00	Example of the present invention
11	7.47	7.78	7.24	Reference Example

[Table 3]

No.	Maximum length of Ti-based inclusions (μm)			Description
	Top	Intermediate	Bottom	
1	7.15	7.00	7.04	Example of the present invention
11	7.55	7.79	7.71	Reference Example

[0063] As shown in Tables 2 and 3, the maximum length of the Ti-based inclusions is smaller for Example No. 1 of the present invention, in which the He gas was introduced, for all the locations of the top, intermediate, and bottom portions. In the case of Reference Example 11, coarse Ti-based inclusions as coarse as about 7.8 μm were observed, while in the Example No. 1 of the present invention, the maximum size of the Ti-based inclusions was about 7.2 μm . Accordingly, it was verified that in producing a maraging steel ingot by vacuum arc remelting, Ti-based inclusions were made finer by introducing the He gas into the gap between the steel ingot and the crucible.

[0064] As a result of comparison among the maximum length of the Ti-based inclusions in the top, intermediate, and bottom portions of the steel ingot, in the case of Reference Example No. 11, the maximum length was irregular ranging from 7.2 μm to 7.8 μm for different locations in the longitudinal and radial directions of the steel ingot (Tables 2 and 3). On the other hand, in the case of Example No. 1 of the present invention, the maximum length was within the range from 7.0 to 7.2 μm for different locations in the longitudinal and radial directions of the steel ingot (Tables 2 and 3). The level of evenness in the size of the Ti-based inclusions for different locations of the steel ingot was high for the case in which the He gas was introduced into the gap between the steel ingot and the crucible.

(Aspect 2)

[0065] In Aspect 2, the diameter of the steel ingot was larger than that in Aspect 1, and it was examined whether the present invention can be applied to the cases of production of large-size steel ingots. In this Aspect, steel ingots were produced under the conditions in which the pressure of the He gas inside the pipe of the vacuum arc remelting apparatus was changed. First, similar to Aspect 1 described above, in the consumable electrode production process, three consumable electrodes for vacuum arc remelting were produced by vacuum melting. In the production of the consumable electrodes, Mg was added to form Mg oxide. In order to examine the presence or absence of Mg oxide, using a method similar to that of Aspect 1, test pieces were sampled from the consumable electrodes for examination as to the presence or absence of Mg oxide, and as a result, the Ti-based inclusions containing MgO as their cores with respect to all the three consumable electrodes. The consumable electrodes were remelted by VAR to produce steel ingots.

[0066] For two electrodes 1 for remelting among the three electrodes, He gas with 99.9 vol. % or higher purity was introduced between the steel ingot 3 and the water-cooled copper crucible 4 during remelting by VAR to produce steel ingots (Examples No. 2 and No. 3 of the present invention). For the other electrode for remelting, the He gas was not introduced between the steel ingot 3 and the water-cooled copper crucible 4 during the vacuum arc remelting (Reference Example No. 12). In both the examples of the present invention and the reference example, the average diameter of the steel ingot was 550 mm.

[0067] The cooling with the He gas was carried out in a way similar to that of Aspect 1. In the cooling with the He gas, the pressure of the He gas inside the pipe was set to 1,300 Pa for Example No. 2 of the present invention and to 1,860 Pa for Example No. 3 of the present invention. The compositions of the electrodes for remelting used in the examples of the present invention and the reference example as well as the compositions of the steel ingot produced by the examples of the present invention and the reference example are shown in Table 4.

[Table 4]

(% by mass)

No.		C	Ni	Mo	Co	Al	Ti	[Mg]	[N]	[O]
2	Electrode	0.0038	18.53	5.00	9.36	0.11	0.47	35	4.6	3.9
	Ingot	0.0040	18.50	4.98	9.35	0.10	0.47	2	3.9	2.3
3	Electrode	0.0037	18.41	4.98	9.31	0.10	0.47	35	5.8	4.7
	Ingot	0.0033	18.46	5.01	9.37	0.10	0.10	3	5.4	2.1
12	Electrode	0.0036	18.43	5.03	9.33	0.11	0.48	34	5.7	4.2
	Ingot	0.0038	18.46	5.03	9.31	0.10	0.48	2	4.9	1.9

The elements other than those shown above are Fe and inevitable impurities. The units for the content of the elements shown with parentheses are ppm.

[0068] Next, the maraging steel remelted by VAR was forged to have a shape of a slab, then in order to sample test pieces from the top, intermediate, and bottom portions for inclusion analysis, the steel ingot was sectioned in the direction normal to the central axis at equal intervals, and test pieces of 2 g a piece were sampled from the steel ingot in the center portions in the radial direction and in the direction of thickness. Because the test pieces for inclusion analysis were sampled after having forged the steel ingot to have a shape of a slab, the distribution of sizes of the Ti-based inclusions containing TiN and TiCN in the radial direction of the steel ingot was not examined. Note that the sizes of the Ti-based inclusions containing TiN, TiCN, and the like were determined by a method similar to that of Example 1, and the Ti-based inclusion largest of all the Ti-based inclusions observed on the filter was used as the inclusion with the maximum length. Table 5 shows the sizes of the Ti-based inclusions containing TiN, TiCN, and the like observed for the top, intermediate, and bottom portions in the slab.

[Table 5]

No.	Pressure of He gas inside the pipe (Pa)	Maximum length of Ti-based inclusions (μm)			Description
		Top	Intermediate	Bottom	
2	1300	7.14	7.00	6.78	Example of the present invention
3	1860	7.23	7.26	6.58	Example of the present invention
12	0	8.47	8.10	7.84	Reference Example

[0069] As shown in Table 5, the maximum length of the Ti-based inclusions was shorter for Examples No. 2 and No. 3 of the present invention, in which the He gas was introduced, for all the locations of the top, intermediate, and bottom portions. In Reference Example No. 12, coarse Ti-based inclusions with the diameter of about 7.5 μm to 8.1 μm were observed. On the other hand, in the examples of the present invention, the largest Ti-based inclusion was 7.26 μm. From the above results, it is obvious that even if the diameter of the steel ingot is large, the Ti-based inclusions are refined due to the cooling effect obtained by introducing He gas.

[0070] Further, the size of the Ti-based inclusions was less uneven in the examples of the present invention, and particularly in Examples No. 2 and No. 3 of the present invention, the maximum length was in the range of 7.0 μm to 7.15 μm and 7.2 μm to 7.3 μm, respectively, for the top and intermediate portions. On the other hand, in Reference Example No. 12, the maximum length of the Ti-based inclusions for the intermediate portion was in the range of 8.1 to 8.5 μm, and the size of the Ti-based inclusions was more uneven compared with the examples of the present invention.

[0071] Table 6 shows the results of calculated amount of released heat when steel ingots were produced in Examples 1 and 2. The amount of released heat was calculated as expressed by the following expression (1) by multiplying the temperature difference between the average value of the temperature of the cooling water introduced into the water-cooled copper crucible and the average value of the temperature of the cooling water drained from the water-cooled copper crucible after having cooled the steel ingot by the flow rate of the cooling water. The temperature of the cooling water used in Example 1 was measured during a time period from the time in which the operation state of the vacuum arc remelting furnace became stabilized, i.e., a timing after 200 minutes had elapsed since the start of the operation, i.e., the timing of start of the remelting, to the time in which the remelting was terminated, i.e., a timing after 500 minutes had elapsed since the start of the operation. On the other hand, the temperature of the cooling water in Example 2 was measured during a time period from the time in which the operation state of the vacuum arc remelting furnace became stabilized, i.e., a timing after 300 minutes had elapsed since the start of the operation, i.e., the timing of start of the remelting, to the time in which the remelting was terminated, i.e., a timing after 1,000 minutes had elapsed since the start of the operation.

[0072] [Equation 1]

$$\text{Heat release amount} = (\text{average value of temperature of drained cooling water} - \text{average value of temperature of introduced cooling water}) \times \text{flow rate} \quad (1)$$

where the units for the temperature of the cooling water: °C; those for the flow rate: L/min

[Table 6]

	Aspect 1		Aspect 2	
	Example 1	Reference Example 11	Example 2	Reference Example 12
Heat release amount (kcal)	2076	1954	2571	2158
Heat release amount (W)	145	136	179	151

[0073] From the results shown in Table 6, it is shown that the amount of released heat in the examples of the present invention, in which the He gas was introduced into the gap between the steel ingot and the crucible, increased compared with those in the reference examples. It is obvious that the cooling water introduced into the water-cooled copper crucible cooled the steel ingot and that the introduced He gas also cooled the steel ingot. The amount of released heat was calculated, and based on the calculated values, the effect of heat release by the He gas was verified.

[0074] From the above results, the size of the Ti-based inclusions differing at different locations of the steel ingot was made more uniform by introducing He gas into the gap between the steel ingot and the crucible and cooling the steel ingot with the He gas. With respect to the slab bottom portion, because it was a portion contacting the bottom of the water-cooled copper crucible 4, the rate of cooling was higher compared with those in the other regions. Accordingly, a synergistic effect between the cooling effect of the crucible and that of the He gas was obtained, and thus the Ti-based inclusions were more refined in the slab bottom portion compared with the top and the intermediate portions of the steel ingot.

[0075] As described above, He gas was introduced into the gap between the steel ingot and the crucible in remelting of the maraging steel by vacuum arc remelting, and thereby it was possible to refine the Ti-based inclusions and suppress unevenness in size of the Ti-based inclusions occurring among different locations of the steel ingot. As a result, the fatigue breaking occurring due to inclusions in maraging steel as the starting point can be prevented, and thereby it is possible to stabilize the quality and the characteristics of maraging steel products.

List of Reference Symbols

[0076]

- 1 Consumable electrode for remelting
- 2 Molten steel pool
- 3 Steel ingot
- 4 Water-cooled copper crucible
- 5 Gas introduction nozzle
- 6 Pressure measuring device
- 7 Pressure control valve
- 8 Piping valve

10 Vacuum arc remelting apparatus
A Rare gas

5 **Claims**

1. A method of producing maraging steel by vacuum arc remelting using a vacuum arc remelting apparatus, comprising:

10 a steel ingot production step of producing a steel ingot by melting a consumable electrode made of a maraging steel containing magnesium oxide in a crucible of the apparatus, wherein during the steel ingot production step, rare gas is introduced between the steel ingot and the crucible to cool the steel ingot.

15 2. The maraging steel production method according to claim 1, wherein the rare gas includes He of 99.9 vol.% or more.

3. The maraging steel production method according to claim 1 or 2, wherein the rare gas is introduced into the crucible via a rare gas introduction pipe, and a pressure of the rare gas inside the rare gas introduction pipe is 100 Pa to 3,000 Pa.

20 4. The maraging steel production method according to any one of claims 1 to 3, wherein an average diameter of the steel ingot is 300 mm to 800 mm.

25 5. The maraging steel production method according to any one of claims 1 to 4, the method further comprising a consumable electrode production step of producing the consumable electrode by vacuum-melting maraging steel and adding magnesium to the maraging steel.

6. A method of refining inclusions in maraging steel by vacuum arc remelting using a vacuum arc remelting apparatus, comprising:

30 a steel ingot production step of producing a steel ingot by melting a consumable electrode constituted by a maraging steel containing magnesium oxide in a crucible of the apparatus, wherein the steel ingot production step includes cooling the steel ingot with rare gas introduced between the steel ingot and the crucible.

35 7. The method of refining inclusions in maraging steel according to claim 6, wherein the rare gas includes He of 99.9 vol.% or more.

40 8. The method of refining inclusions in maraging steel according to claim 6 or 7, the rare gas is introduced into the crucible via a rare gas introduction pipe, and wherein a pressure of the rare gas inside the rare gas introduction pipe is 100 Pa to 3,000 Pa.

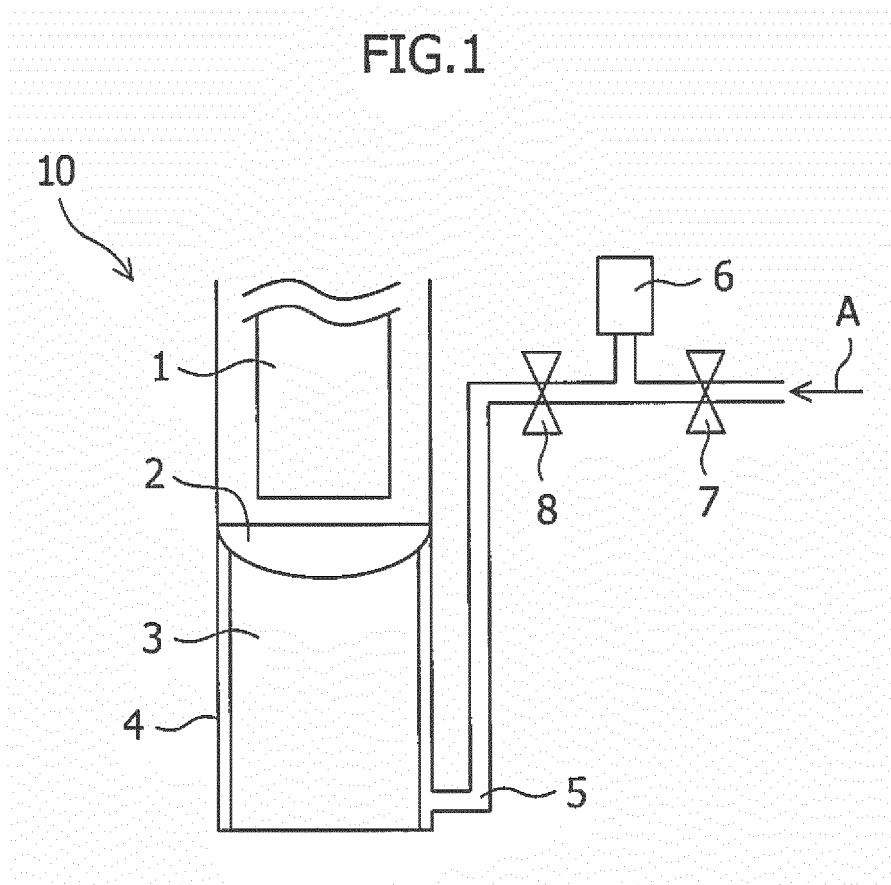
9. The method of refining inclusions in maraging steel according to any one of claims 6 to 8, wherein an average diameter of the steel ingot is 300 mm to 800 mm.

45 10. The method of refining inclusions in maraging steel according to any one of claims 6 to 9, the method further comprising a consumable electrode production step of producing the consumable electrode by vacuum-melting maraging steel by adding magnesium to the maraging steel.

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FIG.1



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2014/057728

A. CLASSIFICATION OF SUBJECT MATTER

C22B9/20(2006.01)i, B22D27/02(2006.01)i, B22D27/04(2006.01)i, C21C7/04
(2006.01)i, C22C38/00(2006.01)i, C22C38/14(2006.01)i

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C22B9/20, B22D27/02, B22D27/04, C21C7/04, C22C38/00, C22C38/14

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Jitsuyo Shinan Koho 1922-1996 Jitsuyo Shinan Toroku Koho 1996-2014

Kokai Jitsuyo Shinan Koho 1971-2014 Toroku Jitsuyo Shinan Koho 1994-2014

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP 2005-232551 A (Hitachi Metals, Ltd.), 02 September 2005 (02.09.2005), claims; paragraphs [0002] to [0008], [0032], [0033] (Family: none)	1-10
Y	JP 2004-90022 A (Hitachi Metals, Ltd.), 25 March 2004 (25.03.2004), claims; paragraphs [0005], [0009] to [0012] (Family: none)	1-10
Y	US 3353585 A (WENTZELL M. Joseph), 21 November 1967 (21.11.1967), column 2, line 35 to column 4, line 15; fig. 1 (Family: none)	1-10

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

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Date of the actual completion of the international search
21 May, 2014 (21.05.14)

Date of mailing of the international search report
03 June, 2014 (03.06.14)

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2014/057728

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	DE 10208903 A1 (ALD Vacuum Technologies AG), 18 September 2003 (18.09.2003), paragraph [0012]; drawings (Family: none)	1-10
Y	JP 9-29420 A (Kobe Steel, Ltd.), 04 February 1997 (04.02.1997), claims; paragraphs [0012], [0014]; fig. 1 (Family: none)	1-10
A	JP 2004-183097 A (Hitachi Metals, Ltd.), 02 July 2004 (02.07.2004), entire text & US 2004/0093983 A1 & EP 1422301 A1 & EP 1826282 A1 & DE 60319197 D & DE 60331111 D	1-10

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REFERENCES CITED IN THE DESCRIPTION

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