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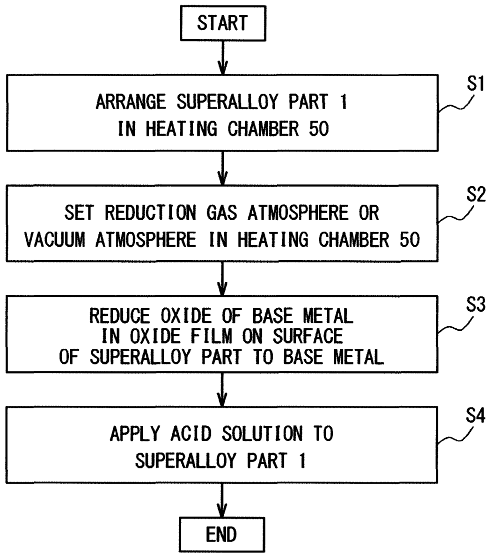
(54) OXIDE FILM REMOVAL METHOD

(57) An oxide film removal method that is a method for removing an oxide film 20 on the surface of a superalloy part 1 that contains a first metal, which is a base metal, and a second metal that differs from the first metal. The oxide film removal method is provided with a step for placing the superalloy part 1 inside a heating chamber 50, a reducing step for reducing oxides of the base metal to the base metal by heating the interior of the heating chamber 50 while maintaining a reducing gas atmosphere or a vacuum atmosphere, and an acid treatment step for applying an acid solution on the superalloy part 1 after the reducing step. The method effectively removes an oxide film on the surface of a superalloy without using highly toxic gaseous fluoride.

Fig. 8



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Description

Technical Field

[0001] The present invention relates to an oxide film removing method, and especially, to a method of removing an oxide film formed in a superalloy surface.

Background Art

[0002] Components of an aircraft engine, a turbine, a plant and so on are sometimes used in a high-temperature environment or a high stress environment. It is known that a part used in the high-temperature environment or the high stress environment is formed of a superalloy material.

[0003] In case of repairing the superalloy part, it is known that an oxide film in the surface of the superalloy part is removed as a pre-process. As the oxide film removing process, the fluoride ion cleaning (FIC) is well-known. However, it is known that hydrogen fluoride gas and so on used for the fluoride ion cleaning is highly toxic.

[0004] As the related technique, Patent Literature 1 discloses a method of cleaning a metal product. The method described in Patent Literature 1 contains removing the surface oxide of the superalloy part by using halide.

[0005] Also, Patent Literature 2 discloses a method of cleaning and repairing a superalloy article. The method described in Patent Literature 2 contains reducing an oxide in a crack of the superalloy part by using gaseous active fluoride ions.

[0006] Also, Patent Literature 3 discloses a method in place of fluoride ion cleaning. The method described in Patent Literature 3 contains expanding a narrow crack, removing a part of metal oxide with an acid solution, and removing a part of the metal oxide by cleaning in a high-temperature vacuum atmosphere or a high-temperature hydrogen atmosphere.

Citation List

[0007]

[Patent Literature 1] JP H07-91662B
[Patent Literature 2] US 4,098,450A
[Patent Literature 3] US 2011/0120972A1

Summary of the Invention

[0008] An object of the present invention is to provide an oxide film removing method that can effectively remove an oxide film in a superalloy surface without using a highly toxic gaseous fluoride.

[0009] This object and other objects and profits of the present invention could be easily confirmed from the following description and the attached drawings.

[0010] An oxide film removing method in some embodiments is a method of removing an oxide film formed in a surface of a superalloy part that contains a first metal as a base metal and a second metal different from the first metal. The oxide film contains oxide of the base metal and oxide of the second metal.

[0011] The oxide film removing method includes arranging the superalloy part inside a heating chamber; preparing a reduction gas atmosphere or a vacuum atmosphere inside the heating chamber; reducing the oxide of the base metal of an oxide film to the base metal by heating the inside of the heating chamber in a condition that the reduction gas atmosphere or the vacuum atmosphere is maintained; and carrying out acid processing to apply acid solution to the superalloy part after the reduction. The acid processing includes: dissolving the base metal; and separating the oxide of the second metal left without being reduced through the reduction from the superalloy part together with the dissolved base metal.

[0012] In the oxide film removing method, the acid processing may not be carried out before the reduction.

[0013] In the oxide film removing method, the base metal may be nickel or cobalt.

[0014] In the oxide film removing method, the oxide of the second metal is a metal oxide in which thermodynamic stability is higher than that of the oxide of the base metal.

[0015] In the oxide film removing method, the second metal may contain at least one of aluminum, titanium, and chrome.

[0016] In the oxide film removing method, the second metal may contain aluminum.

[0017] In the oxide film removing method, the acid solution may contain hydrochloric acid.

[0018] In the oxide film removing method, the superalloy part may have a crack, and the oxide film may contain an oxide film formed in a surface of the crack.

[0019] In the oxide film removing method, the method may not contain expanding a crack physically.

[0020] In the oxide film removing method, the method may not contain a fluoride ion cleaning process.

[0021] According to the present invention, the oxide film removing method can be provided in which the oxide film in the superalloy surface can be effectively removed without using a highly toxic gaseous fluoride.

Brief Description of the Drawings

[0022]

[FIG. 1]
FIG. 1 is a sectional view schematically showing an example of a superalloy part.
[FIG. 2]
FIG. 2 is a sectional view schematically showing the superalloy part after nickel oxide is reduced to nickel.
[FIG. 3]
FIG. 3 is a sectional view schematically showing the superalloy part 1 during application of hydrochloric

acid solution.

[FIG. 4]

FIG. 4 is a sectional view schematically showing the superalloy part 1 during application of hydrochloric acid solution.

[FIG. 5]

FIG. 5 is a sectional view schematically showing an example of the superalloy part.

[FIG. 6]

FIG. 6 is a sectional view schematically showing an example of a reduction processing device.

[FIG. 7]

FIG. 7 is a sectional view schematically showing an example of an acid processing device.

[FIG. 8]

FIG. 8 is a flow chart showing a procedure of removing an oxide film.

[FIG. 9A]

FIG. 9A shows an experiment result showing the effectivity of an oxide film removing method according to an embodiment.

[FIG. 9B]

FIG. 9B shows the experimental result showing the effectivity of the oxide film removing method according to the embodiment.

[FIG. 9C]

FIG. 9C shows the experimental result showing the effectivity of the oxide film removing method according to the embodiment.

Description of the Embodiments

[0023] Hereinafter, an oxide film removing method according to an embodiment will be described with reference to the attached drawings.

(Definition of important terms)

[0024] In this Specification, "Superalloy" means alloy usable (in other words, sustainable in strength) in a high temperature environment (e.g. 800 °C or above).

[0025] In this Specification, a "base metal" means a metal component with the highest content (weight %) of the metal components contained in alloy.

(Overview of oxide film removing method)

[0026] As an example, a method of removing an oxide film formed in the surface of a superalloy part that contains nickel (Ni) as a base metal and aluminum (Al) will be described.

[0027] FIG. 1 is a sectional view schematically showing an example of a superalloy part 1. The superalloy part 1 contains a base material 10 and an oxide film 20. The oxide film 20 is formed by, for example, exposing the superalloy part 1 to air (oxygen) under the high-temperature environment. Note that a boundary between the base material 10 and the oxide film 20 is clearly illustrated in FIG. 1. However, in actual, the boundary between the base material 10 and the oxide film is not always definite.

[0028] The base material 10 is superalloy that contains base metal and second metal. In an example shown in FIG. 1, the base metal is nickel and the second metal is aluminum.

[0029] The oxide film 20 contains the oxide of base metal and the oxide of second metal. In the example shown in FIG. 1, the oxide of base metal is nickel oxide (e.g. NiO). Also, the oxide of second metal is aluminum oxide (e.g. Al_2O_3). In FIG. 1, a region 22 where nickel oxide is rich (in other words, a region where the concentration of nickel oxide is relatively high) is schematically shown by a symbol of a white triangle. Also, in FIG. 1, a region 24 where aluminum oxide is rich (in other words, the region where the concentration of aluminum oxide is relatively high) is schematically shown by a symbol of a white circle.

[0030] When the superalloy part 1 shown in FIG. 1 is arranged in a high temperature reduction gas atmosphere or a high temperature vacuum atmosphere, nickel oxide is reduced to nickel. FIG. 2 is a sectional view schematically showing the superalloy part 1 after nickel oxide is reduced to nickel.

[0031] In FIG. 2, a region 32 where nickel has become rich through the reduction is schematically shown by a symbol of black triangle. Note that although not illustrated to FIG. 2, nickel oxide that exists in the region 24 where aluminum oxide is rich has also been reduced to nickel.

[0032] On the other hand, since aluminum oxide is a compound that is stable thermodynamically, the state of oxide is maintained even if the aluminum oxide is arranged in the high-temperature reduction gas atmosphere or the high-temperature vacuum atmosphere. Therefore, the aluminum oxide is difficult to be reduced more than the nickel oxide.

[0033] When hydrochloric acid solution to the superalloy part 1 shown in FIG. 2 is applied, the region 32 where nickel is rich is dissolved with the hydrochloric acid solution (more specifically, nickel in the region where nickel is rich is dissolved by the hydrochloric acid solution). Also, the hydrochloric acid solution enters a cavity (or a passage) formed through the dissolving of nickel. As a result, nickel in a region other than the region 32 where nickel is rich (for example, nickel in the region 24 where aluminum oxide is rich) is also dissolved by the hydrochloric acid solution.

[0034] FIG. 3 is a sectional view schematically showing the superalloy part 1 during application of the hydrochloric acid solution. Referring to FIG. 3, it is understood that the region 32 where nickel is rich disappears through the dissolution and a cavity 42 (or a passage) is formed. Also, it could be understood that a smaller cavity 43 (or a passage) is formed from the cavity 42. Due to existence of the cavity 42 and the cavity 43, bonding force between a portion of the oxide film 20 and another portion of the oxide film 20, and bonding force between the oxide film 20 and the base material 10 are reduced.

[0035] FIG. 4 is a sectional view schematically showing the superalloy part 1 during the application of hydrochloric acid solution, and showing the state after a time passed from the state shown in FIG. 3. Referring to FIG. 4, it could be understood that the aluminum oxide (or the region 24 where aluminum oxide is rich) is separated from the superalloy part 1 (or the base material 10) together with the dissolved nickel, due to the reduction of bonding force between the oxide film 20 and the base material 10.

[0036] Note that even if the hydrochloric acid solution is applied to the superalloy part shown in FIG. 1, the cavity 42 or cavity 43 as shown in FIG. 3 is difficult to be formed, since the nickel oxide is difficult to be dissolved with the hydrochloric acid solution more than nickel. On the other hand, in the present embodiment, since the oxide of base metal is reduced to the base metal before the application of hydrochloric acid solution, the cavity 42 or cavity 43 as shown in FIG. 3 is easy to be formed. As a result, as shown in FIG. 4, the aluminum oxide that is difficult to be reduced becomes able to be separated from the superalloy part 1 (or the base material 10).

[0037] In an example shown in FIG. 1 to FIG. 4, it is possible to effectively separate and remove the oxide film in the surface of superalloy part without using gaseous fluoride having strong toxic.

[0038] In the example shown in FIG. 1 to FIG. 4, a case that the base metal is nickel has been described. However, the base metal is not limited to nickel. For example, the base metal may be cobalt.

[0039] In the example shown in FIG. 1 to FIG. 4, a case that the second metal contained in the superalloy part 1 is aluminum has been described. However, the second metal is not limited to aluminum. The second metal may be chrome or titanium. Alternatively, the second metal may contain at least one of aluminum, titanium, and chrome. For example, the second metal may contain aluminum and chrome.

[0040] In the example shown in FIG. 1 to FIG. 4, a case that acid solution is hydrochloric acid solution has been described. However, the acid solution is not limited to the hydrochloric acid solution, and is optional. The acid solution may be an acid solution of whatever kind if the acid solution can dissolve the base metal. Also, the acid solution may be mixed acid (for example, the mixed acid of hydrochloric acid and nitric acid).

(More detailed description of oxide film removing method)

[0041] Referring to FIG. 5 to FIG. 8, the oxide film removing method according to an embodiment will be described in detail.

(Superalloy part)

[0042] FIG. 5 is a sectional view schematically showing an example of the superalloy part 1. The oxide film 20 is formed in the surface of the superalloy part 1. The oxide film 20 may be formed in the whole surface of the superalloy part 1 and may be formed in a part of the surface of the superalloy part 1.

[0043] For example, the superalloy part 1 is a superalloy part that has a crack 3. In the example shown in FIG. 5, the oxide film 20 is formed in the surface of crack 3, too.

[0044] For example, the base metal of the superalloy part 1 is nickel. In other words, of the metal components contained in the superalloy part 1, a first metal with the highest content weight% is, for example, nickel. The superalloy part 1 may be a nickel-based superalloy part (in other words, the superalloy part in which the content of the nickel is 50 weight% or above). For example, aluminum may be contained as the alloy component in the superalloy part 1. In other words, of the metal components contained in the superalloy part 1, the second metal that is different from the first metal is, for example, aluminum.

[0045] The oxide of base metal (e.g. nickel) and the oxide of second metal (e.g. aluminum) are contained in the oxide film in the surface of superalloy part 1.

(Reduction processing device)

[0046] FIG. 6 is a sectional view schematically showing an example of the reduction processing device 5. The reduction processing device 5 includes, for example, a main unit section 51, a door 52, a heater 53, a temperature sensor 54, a controller 55, a gas supply pipe 56, a first valve 57, a gas discharge pipe 58, and a second valve 59.

[0047] The main unit section 51 accommodates the superalloy part 1 as an object to be processed. The door 52 opens and closes an opening of the main unit section 51. The main unit section 51 and the door 52 functions as a heating chamber 50 when the superalloy part 1 is to be reduction processed (more specifically, a heating sealed chamber).

[0048] The heater 53 is a device for heating the heating chamber 50. In other words, the heater 53 is a device for heating the heating chamber or the superalloy part 1 arranged in the heating chamber. The temperature sensor 54 is a sensor to measure a temperature in the heating chamber or a temperature of the superalloy part 1. Data acquired by the temperature sensor 54 is sent to the controller 55. The controller 55 controls the heater 53 based on the data received from the temperature sensor 54. By controlling the heater 53 by the controller 55, the temperature in the heating chamber or the temperature of the superalloy part 1 is maintained in a desired temperature.

[0049] The gas supply pipe 56 is used to supply reduction gas into the heating chamber 50. The first valve 57 is arranged in the passage of gas supply pipe 56 and opens and closes the passage. For example, the reduction gas is hydrogen gas. Note that when the reduction processing device 5 is a device which carries out the reduction processing in a vacuum atmosphere, the gas supply pipe 56 and the first valve 57 may be omitted.

[0050] The gas discharge pipe 58 is used to discharge air (gas) from the heating chamber 50. For example, the gas discharge pipe 58 is connected with a vacuum pump (not illustrated). The second valve 59 is arranged in the passage of gas discharge pipe 58 and opens and closes the passage.

(Acid processing device)

[0051] FIG. 7 is a sectional view schematically showing an example of the acid processing device 6. For example, the acid processing device 6 has a liquid bath 60. Acid solution 62 is filled in the liquid bath 60. The superalloy part 1 as the object to be processed is arranged in the liquid bath 60.

(Procedure of removing oxide film)

[0052] Next, referring to FIG. 8, a procedure of removing the oxide film will be described. FIG. 8 is a flow chart showing the procedure of removing the oxide film.

[0053] At a first step S1, the superalloy part 1 that contains nickel (first metal) as the base metal and aluminum (second metal different from nickel) is arranged in the heating chamber 50.

[0054] Note that the oxide film 20 is formed in the surface of the superalloy part 1. Also, the oxide film 20 contains nickel oxide (the oxide of base metal) and aluminum oxide (the oxide of second metal).

[0055] At a second step S2, a reduction gas atmosphere or a vacuum atmosphere is prepared in the heating chamber 50.

[0056] When preparing the reduction gas atmosphere, the gas in the heating chamber 50 is first discharged through the gas discharge pipe 58. After that, the reduction gas is supplied into the heating chamber 50 through the gas supply pipe 56. For example, the reduction gas is hydrogen (H_2) gas. When the reduction gas is hydrogen gas, the grade of hydrogen gas to be supplied into the heating chamber 50 is, for example, G1 equivalent (in other words, the purity of hydrogen gas is 99.99999 volume % or above). When the reduction gas is the hydrogen gas, for example, the dew point in the heating chamber 50 after introduction of the reduction gas is equal to or less than -80 °C.

[0057] Alternatively, when the vacuum atmosphere should be prepared, the gas in the heating chamber 50 is discharged through the gas discharge pipe 58. For example, through the discharge, the pressure in the heating chamber 50 is lowered to 10^{-3} Pa or below.

[0058] A third step S3 is a reduction step of reducing the oxide of base metal to the base metal. At the third step S3, the inside of the heating chamber 50 is heated in the condition that the reduction gas atmosphere or the vacuum atmosphere is maintained. The temperature in the heating chamber is maintained at, for example, 800 °C or above, 1000 °C or above, 1100 °C or above (especially, in case of the vacuum atmosphere), or 1200 °C or above. Also, the temperature in the heating chamber is maintained below the melting point of superalloy that configures the superalloy part. The heating processing time is, for example, from 15 minutes to 24 hours, from 30 minutes to 24 hours, or from 60 minutes to 24 hours. For example, the temperature in the heating chamber is 1000 °C or above and the melting point of superalloy or below, and the heating processing time is from 30 minutes or above to 300 minutes or below.

[0059] By executing the third step S3 as the reduction step, nickel oxide (the oxide of base metal) is reduced to nickel (the base metal) of the oxide contained in the surface oxide film of the superalloy part 1. After the third step S3 is executed, the superalloy part 1 is taken out from the heating chamber 50.

[0060] A fourth step S4 is an acid processing step. At the fourth step S4, the acid solution is applied to the superalloy part 1. The application of acid solution to the superalloy part 1 is carried out by, for example, immersing the superalloy part 1 in the acid solution 62 in the liquid bath 60.

[0061] When the base metal is nickel, it is desirable that the acid solution contains hydrochloric acid. This is because nickel has a high solubility to the hydrochloric acid. Iron chloride (III) ($FeCl_3$) may be contained in the acid solution. Iron chloride (III) reinforces oxidizability of the hydrochloric acid. Alternatively or additionally, nitric acid may be contained in the acid solution. For example, the acid solution may be a solution that contains the hydrochloric acid, the iron chloride (III) and the nitric acid.

[0062] The temperature of acid solution is, for example, 10 °C or above and 40 °C or below, 10 °C or above and 30 °C or below, or 20 °C or above and 30 °C or below.

[0063] The processing time of the acid processing step (in other words, a time during which the superalloy part 1 is immersed in the acid solution) is, for example, 20 minutes or above to 180 minutes or below, 30 minutes or above to 180 minutes or below, 40 minutes or above to 180 minutes or below.

[0064] Through execution of the fourth step S4 as the acid processing step, nickel (the base metal) that exists in the surface of the superalloy part 1 is dissolved by the acid solution. In other words, nickel (the base metal) generated from nickel oxide (the oxide of base metal) in the oxide film 20 by the reduction step is dissolved by the acid solution.

[0065] Also, by execution of the fourth step S4 as the acid processing step, the aluminum oxide (the oxide of second metal) left without being reduced at the reduction step is separated from the superalloy part 1 together with the dissolved base metal. After the execution of the fourth step S4, the superalloy part 1 is taken out from the acid solution and washed (e.g. with water).

[0066] The oxide film 20 is effectively removed from the superalloy part 1 through the above steps.

[0067] Note that the superalloy part 1 processed by the above steps is a superalloy part having a crack 3. In an example shown in FIG. 5, the oxide film 20 is formed in the surface of the crack 3, too. For removal of the oxide film in the surface of crack 3, a physical method such as polishing cannot be sometimes applied. In such a case, the oxide film removing method in the present embodiment is effective. When the oxide film removing method in the present embodiment is used, a step of physically expanding the crack 3 by the polishing and so on is unnecessary.

[0068] When the superalloy part 1 to be processed by the above steps is a superalloy part having the crack 3, the crack 3 may be repaired, after the oxide film removing method in the present embodiment is executed (in other words, after execution the above-mentioned first to fourth steps). For example, the repair of the crack 3 is executed by filling a brazing material into the crack 3. For example, as the brazing material, the brazing material having the base metal of the superalloy part 1 as a main component can be used. For example, when the base metal of the superalloy part 1 is nickel, nickel-based brazing material is used, and when the base metal of the superalloy part 1 is cobalt, cobalt-based brazing material can be used.

[0069] For example, the superalloy part 1 may be a superalloy part which has been used in the high-temperature environment of equal to or more than 800 °C. The crack and so on is easy to be caused due to heat fatigue in the superalloy part which has been used in the high-temperature environment. Also, the oxide film in the surface of the superalloy part has a low solubility to the acid solution due to the exposure to the high-temperature environment. Therefore, it is sometimes difficult to remove the oxide film only by the acid processing. In such a case, the oxide film removing method in the present embodiment is effective.

[0070] Aluminum oxide, titanium oxide or chrome oxide may be contained in the oxide film 20 in the surface of the superalloy part 1. The aluminum oxide, the titanium oxide and the chrome oxide are oxides difficult to reduce, compared with the nickel oxide. The aluminum oxide, the titanium oxide and the chrome oxide are not reduced by the reduction step of the above-mentioned third step. Therefore, when the aluminum oxide, the titanium oxide or the chrome oxide is contained in the oxide film 20 in the surface of the superalloy part 1, the oxide film removing method in the present embodiment is effective in which the acid processing step is executed after the reduction step.

[0071] Note that the thermodynamic stability of the metal oxide is $Al_2O_3 > TiO_2 > Cr_2O_3 > CoO > NiO$ in descending order at 1200 °C. Therefore, generally, the reduction is difficult in the order of the aluminum oxide, the titanium oxide, the chrome oxide, the cobalt oxide, and the nickel oxide.

[0072] To remove the aluminum oxide and so on, the strong reducer of gaseous fluoride (e.g. HF gas) is sometimes used. However, the gaseous fluoride has high toxicity. Also, the gaseous fluoride sometimes gives damage to the boundary between crystals of the superalloy. Moreover, the superalloy part sometimes corrodes due to the gaseous fluoride remained after reduction processing. In addition, a special facility is necessary for the application of the gaseous fluoride. On the other hand, according to the oxide film removing method in the present embodiment, it is possible to remove the aluminum oxide and so on without reducing it. For this reason, it is possible to avoid and reduce the use of the strong reducer such as the gaseous fluoride.

[0073] FIG. 9A to FIG. 9C are experiment data showing the effectivity of the oxide film removing method in the present embodiment.

[0074] In the experiment, a superalloy sample was used in which the base metal was nickel and aluminum and chrome were contained. In case of experiment, first, the superalloy sample was oxidized in the atmosphere.

[0075] The surface state of the superalloy sample after the oxidation was analyzed by using an X-ray photoelectron spectroscopy. FIG. 9A is a graph showing the analysis result. In the graph of FIG. 9A, the horizontal axis shows a depth (nanometer) from the surface of the superalloy sample, and the vertical axis shows detection strength (the number of detected photoelectrons).

[0076] Referring to FIG. 9A, it could be found that nickel oxide, aluminum oxide and chrome oxide are formed in the surface of the superalloy sample (the region from 0 nm to 1600 nm in depth from the surface of the sample). Also, it could be found that metal nickel exists hardly in the region from 0 nm to 800 nm in depth from the surface of the sample.

[0077] Next, the superalloy sample after the above-mentioned oxidation is reduced at the above-mentioned third step S3. The state of the surface of the superalloy sample after the reduction is analyzed by using the X-ray photoelectron spectroscopy. FIG. 9B is a graph showing the analysis result. In the graph of FIG. 9B, the horizontal axis shows a depth (nanometer) from the surface of the superalloy sample, and the vertical axis shows detection strength (the number of detected photoelectrons).

[0078] Referring to FIG. 9B, it could be found that aluminum oxide and chrome oxide exist in the surface section of the superalloy sample (the region from 0 nm to 1600 nm in depth from the surface of the sample). In other words, it could be found that aluminum oxide and chrome oxide are not too much reduced in the reduction processing.

[0079] Also, referring to FIG. 9B, it could be found that metal nickel exists in the region from 0 nm to 800 nm in depth from the surface of the sample. In other words, it could be found that the nickel oxide existing in the region from 0 nm to 800 nm in depth from the surface of the sample was reduced to metal nickel. Also, it could be found that since nickel oxide was hardly observed in the region from 800 nm to 1600 nm in depth from the surface of the sample, the nickel oxide that had existed in the region from 800 nm to 1600 nm in depth from the surface of the sample has also been reduced to metal nickel.

[0080] As mentioned above, it was proved that at the reduction step in the present embodiment, the nickel oxide which is the oxide of base metal was effectively reduced but aluminum oxide and chrome oxide were not effectively reduced.

[0081] Next, the superalloy sample after the above-mentioned reduction processing is acid processed at the above-mentioned fourth step S4. The state of the surface of the superalloy sample after acid processing is analyzed by using the X-ray photoelectron spectroscopy. FIG. 9C is a graph showing the analysis result. In the graph of FIG. 9C, the horizontal axis shows a depth (nanometer) from the surface of the superalloy sample, and the vertical axis shows detection strength (the number of detected photoelectrons).

[0082] Referring to FIG. 9C, it could be found that aluminum oxide and chrome oxide exist hardly in the surface (the region from 0 nm to 1600 nm in depth from the surface of the superalloy sample). It is found from the above fact that the oxide films that had existed in the surface of the superalloy sample after the reduction processing have disappeared after the acid processing. Note that the aluminum oxide is insoluble to the acid solution. Therefore, the disappearance of the oxide film is inferred not to be caused by the dissolving of aluminum oxide. It is inferred that the disappearance of the oxide film is caused as the result that nickel in the oxide film dissolved so that aluminum oxide (and chrome oxide) lost a base to combine with the superalloy sample.

[0083] As mention above, it was proved that the oxide film was removed effectively by executing the acid processing after the reduction processing.

[0084] Note that the oxide film was formed when the superalloy part was exposed to air (oxygen) under the high-temperature environment. The oxide film becomes difficult to dissolve by the acid when the oxide film is exposed to air in the high-temperature environment. Therefore, it is desirable that the reduction processing is executed before the acid processing, in order to remove the oxide film effectively. In some embodiments, the reduction processing is executed before the acid processing. Therefore, in some embodiments, the oxide film can be removed more effectively, compared with a case of execute the reduction processing after the acid processing.

[0085] The present invention is not limited to the above embodiments, and it would be apparent that the embodiments may be changed or modified appropriately in a range of the technique thought of the present invention. Also, various techniques used in each of the embodiments or modification examples can be applied to another embodiment or modification example, as long as any technical contradiction does not occur.

Claims

1. An oxide film removing method of removing an oxide film formed in a surface of a superalloy part that contains a first metal as a base metal and a second metal different from the first metal, the oxide film containing oxide of the base metal and oxide of the second metal,
   the oxide film removing method comprising:

   arranging the superalloy part inside a heating chamber;
   preparing a reduction gas atmosphere or a vacuum atmosphere inside the heating chamber;
   reducing the oxide of the base metal of the oxide film to the base metal by heating the inside of the heating chamber in a condition that the reduction gas atmosphere or the vacuum atmosphere is maintained; and
   carrying out acid processing to apply acid solution to the superalloy part after the reduction,
   wherein the acid processing comprises:

   dissolving the base metal; and
   separating the oxide of the second metal left without being reduced through the reduction, from the superalloy part together with the dissolved base metal.

2. The oxide film removing method according to claim 1, wherein the acid processing is carried out after the reduction.

3. The oxide film removing method according to claim 1 or 2, wherein the base metal is nickel or cobalt.

4. The oxide film removing method according to any one of claims 1 to 3, wherein the oxide of the second metal is a metal oxide in which thermodynamic stability is higher than that of the oxide of the base metal.

5. The oxide film removing method according to any one of claims 1 to 4, wherein the second metal contains at least one of aluminum, titanium, and chrome.

6. The oxide film removing method according to claim 5, wherein the second metal contains aluminum.

7. The oxide film removing method according to any one of claims 1 to 6, wherein the acid solution contains hydrochloric acid.

8. The oxide film removing method according to any one of claims 1 to 7, wherein the superalloy part has a crack, and
   wherein the oxide film contains an oxide film formed in a surface of the crack.

9. The oxide film removing method according to claim 8, wherein the method does not contain expanding a crack physically.

10. The oxide film removing method according to any one of claims 1 to 9, wherein the method does not contain a fluoride ion cleaning process.

Fig. 1

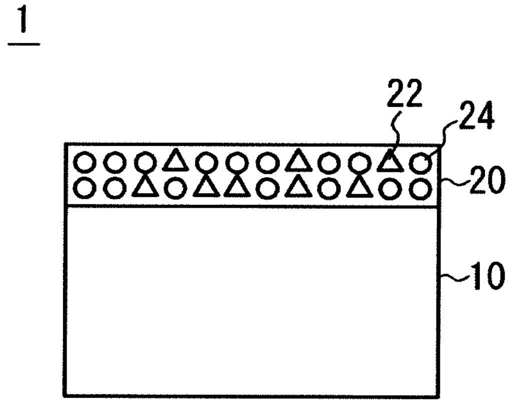


Fig. 2

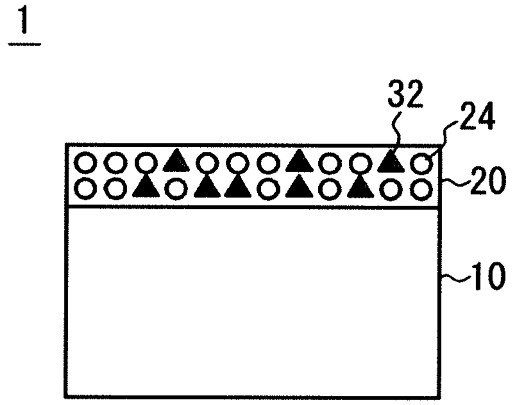


Fig. 3

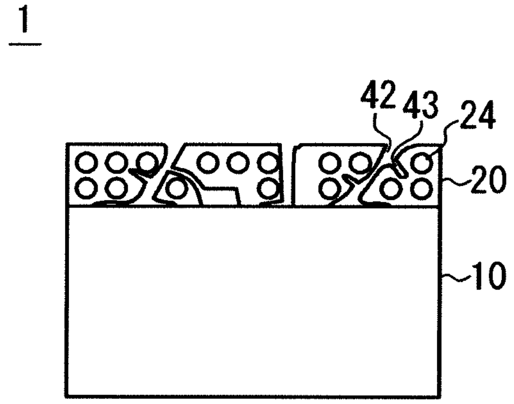


Fig. 4

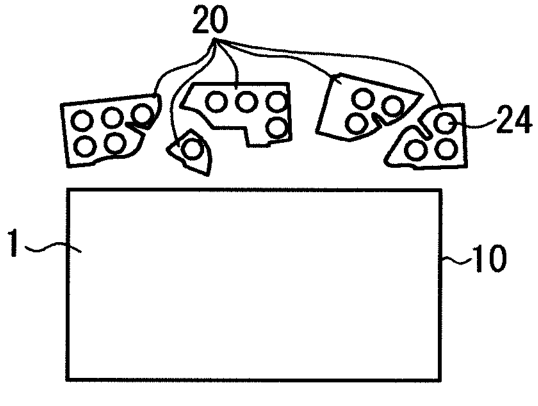


Fig. 5

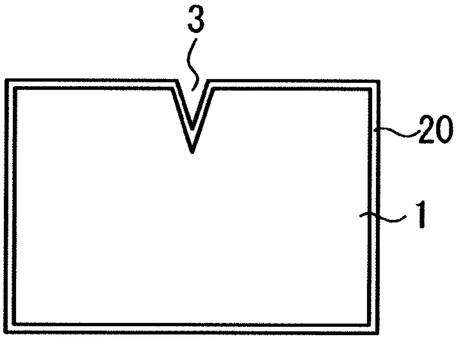


Fig. 6

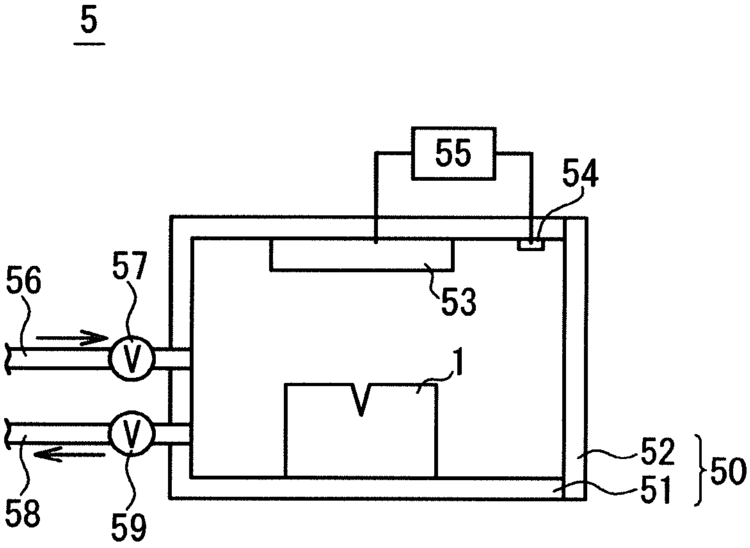


Fig. 7

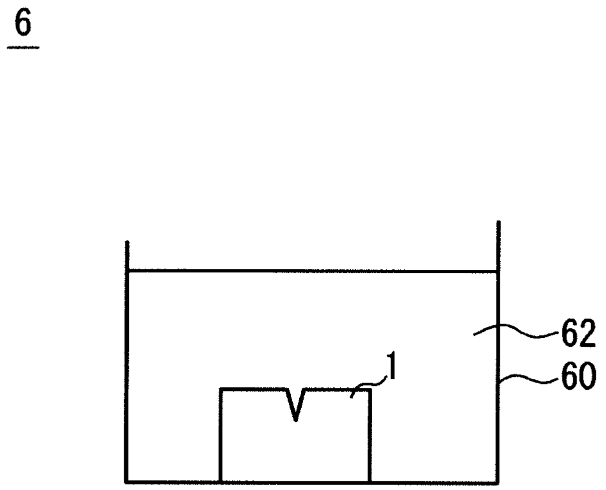


Fig. 8

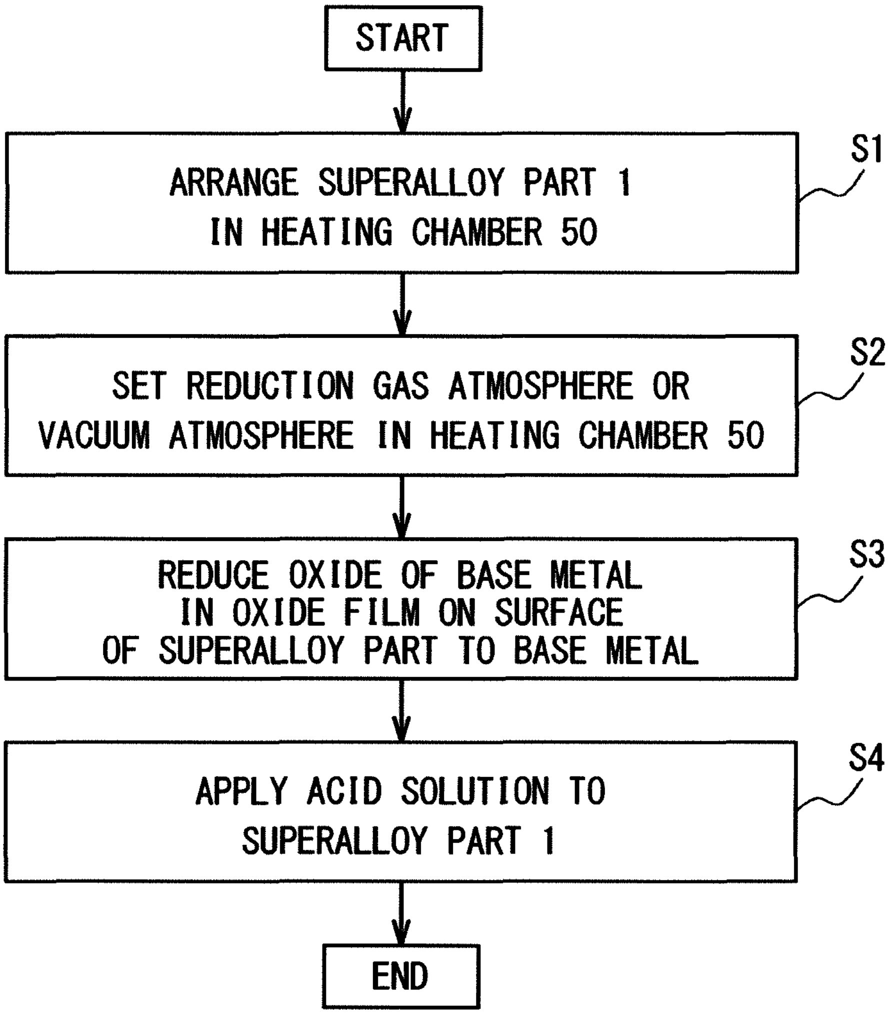

START
ARRANGE SUPERALLOY PART 1 IN HEATING CHAMBER 50
S1
SET REDUCTION GAS ATMOSPHERE OR VACUUM ATMOSPHERE IN HEATING CHAMBER 50
S2
REDUCE OXIDE OF BASE METAL IN OXIDE FILM ON SURFACE OF SUPERALLOY PART TO BASE METAL
S3
APPLY ACID SOLUTION TO SUPERALLOY PART 1
S4
END

Fig. 9A

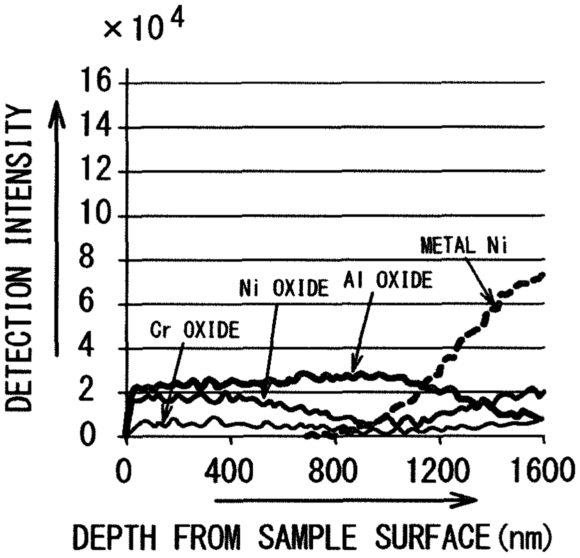

×10⁴
DETECTION INTENSITY
16
14
12
10
8
6
4
2
0
Cr OXIDE
Ni OXIDE
Al OXIDE
METAL Ni
0
400
800
1200
1600
DEPTH FROM SAMPLE SURFACE (nm)

Fig. 9B

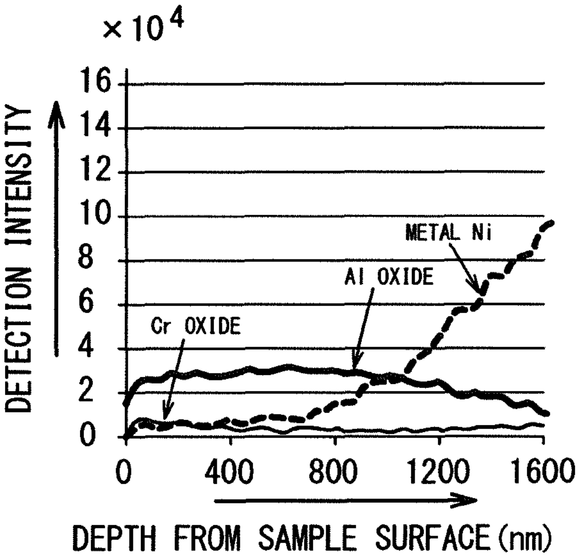
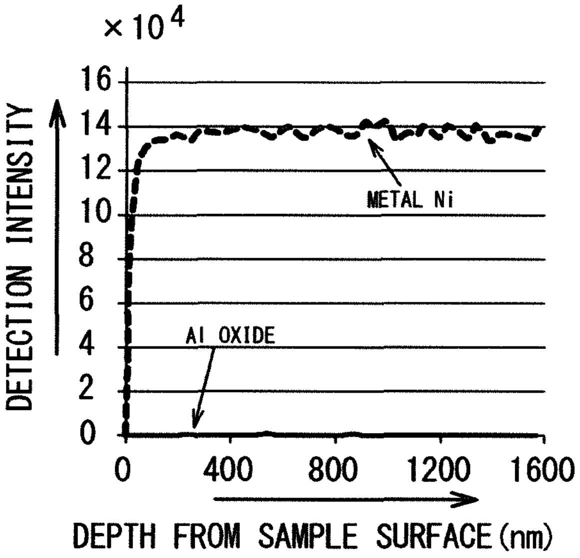

×10⁴
DETECTION INTENSITY
16
14
12
10
8
6
4
2
0
Cr OXIDE
Al OXIDE
METAL Ni
0
400
800
1200
1600
DEPTH FROM SAMPLE SURFACE (nm)

Fig. 9C


×10^4
16
14
12
10
8
6
4
2
0
DETECTION INTENSITY
METAL Ni
Al OXIDE
0
400
800
1200
1600
DEPTH FROM SAMPLE SURFACE (nm)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2016/063267

A. CLASSIFICATION OF SUBJECT MATTER
C23G5/00(2006.01)i, *C23F1/00*(2006.01)i, *C23F1/28*(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)
C23G5/00, C23F1/00, C23F1/28

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	1996-2016
Kokai Jitsuyo Shinan Koho	1971-2016	Toroku Jitsuyo Shinan Koho	1994-2016

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	US 2005/0035085 A1 (STOWELL William Randolph et al.), 17 February 2005 (17.02.2005), claim 1; paragraphs [0001], [0011] to [0043] (Family: none)	1-10
Y	JP 7-290280 A (Nippon Steel Corp.), 07 November 1995 (07.11.1995), paragraphs [0007] to [0015] (Family: none)	1-10

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

* Special categories of cited documents:
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"P" document published prior to the international filing date but later than the priority date claimed
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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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"&" document member of the same patent family

Date of the actual completion of the international search 14 July 2016 (14.07.16)	Date of mailing of the international search report 26 July 2016 (26.07.16)
Name and mailing address of the ISA/ Japan Patent Office 3-4-3,Kasumigaseki,Chiyoda-ku, Tokyo 100-8915,Japan	Authorized officer Telephone No.

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2016/063267

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 63-26343 A (United Technologies Corp.), 03 February 1988 (03.02.1988), entire text & US 4729799 A whole document & EP 251983 A1 & DE 3761024 D & MX 168891 B & AU 7498987 A & IL 82952 A & CA 1299070 A & SG 5490 G & KR 10-1993-0003644 B	1-10
A	JP 1-195290 A (BBC Brown Boveri AG), 07 August 1989 (07.08.1989), entire text & US 4944807 A whole document & EP 318724 A1 & DE 3879634 A & CH 674851 A	1-10
A	US 2011/0120972 A1 (MEYER TOOL, INC.), 26 May 2011 (26.05.2011), whole document (Family: none)	1-10

Form PCT/ISA/210 (continuation of second sheet) (January 2015)

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- JP H0791662 B **[0007]**
- US 4098450 A **[0007]**
- US 20110120972 A1 **[0007]**