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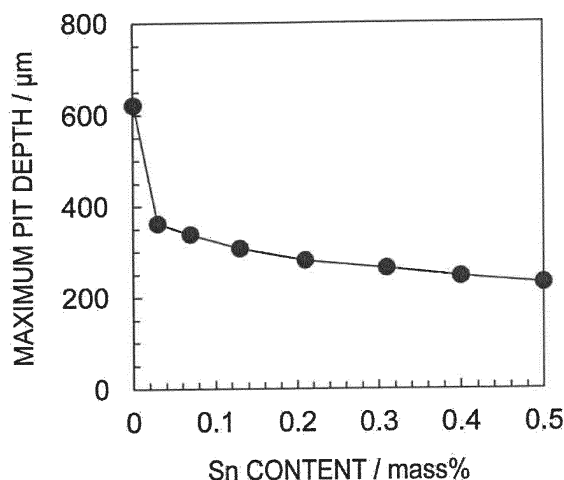
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(54) **FERRITIC STAINLESS STEEL FOR EXHAUST SYSTEM MEMBER HAVING EXCELLENT CORROSION RESISTANCE AFTER HEATING**

(57) A ferritic stainless steel for exhaust system components excellent in corrosion resistance after heating is provided. A ferritic stainless steel for exhaust system components excellent in corrosion resistance after heating includes: 0.015 mass% or less of C; 0.02 mass% or less of N; 0.03 mass% to 1.0 mass% of Si; 1.0 mass% of Mn; 0.04 mass% of P; 0.01 mass% of S; 10.5 mass% to 22.5 mass% of Cr; 0.02 mass% to 0.5 mass% of Sn; 0.003 mass% to 0.2 mass% of Al; one or both of 0.03 mass% to 0.35 mass% of Ti and 0.03 mass% to 0.6 mass% of Nb; and a remnant comprising Fe and inevitable impurities, wherein a grain size number on a surface of the ferritic stainless steel is 6 to 2 to 15 nm of a layer containing Sn at a concentration twice or more of Sn content in the base material is formed on the ferritic stainless steel.

FIG. 1



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Description

TECHNICAL FIELD

[0001] The present invention relates to a ferritic stainless steel excellent in corrosion resistance after heating and suitable for use in an exhaust system component for an automobile, a motor cycle, a commercial vehicle and a construction machine, an exhaust system component and a manufacturing method thereof. Specifically, the present invention relates to a ferritic stainless steel adapted to be heated to 573 to 1073 K to be used with an oxide film being formed on a surface thereof.

BACKGROUND ART

[0002] Ferritic stainless steel is often used for exhaust system components of an automobile, a motor cycle, a commercial vehicle, a construction machine and the like. Especially, downstream exhaust system components (so-called "cold end") are often made of SUH409L steel (a steel containing C and N fixed by Ti and 11% of Cr), SUS430LX steel (a steel containing C and N fixed by Ti and 17% of Cr), and SUS436J1L and SUS436L further added with Mo, in terms of corrosion resistance, formability and weldability.

[0003] In view of recent growing concern over global environment issues, exhaust gas regulations and fuel consumption regulations are tightened every year. Accordingly, various measures have been studied and implemented by automobile manufactures and automobile parts manufactures. It is thus required to increase corrosion resistance or strength of materials to reduce thickness and, consequently, weight of the materials. A demand for a longer guarantee period of the components also necessitates the improvement in corrosion resistance.

[0004] Many of the exhaust system components are subjected to heating when being welded for assembly to generate an oxide film (so-called "temper color") at a welding heat-affected zone (HAZ). The oxide film is sometimes generated during a travel of a vehicle depending on the location of the components. Thus, corrosion resistance of materials with the oxide film being formed is practically important.

[0005] The corrosion resistance herein includes corrosion resistance against condensed water of exhaust gas on an interior surface and corrosion resistance against salt-induced corrosion on an exterior surface. In many cases, reduction in lifetime resulting in breakage due to local thickness reduction and generation of through pit(s) causing leakage of exhaust gas are of problem. Accordingly, pitting resistance bears a high importance in corrosion resistance. In addition, degradation in appearance due to generation of rust has recently been seen as a problem.

[0006] Some solutions have been proposed for the above problems.

[0007] For instance, Patent Literature 1 discloses a stainless steel sheet with improved crevice corrosion resistance, the stainless steel containing 0.015% or less of C, 0.02% or less of N, 1.0% or less of Si, more than 0.6% to 3.0% of Ni, 16.0 to 25.0% of Cr, optionally one or both of 3.0% or less of Mo and 2.0% or less of Cu as necessary, and one or more of 2.0% or less of Mn, 0.5% or less of Ti, 0.5% or less of Nb, 0.5% or less of Al and 0.01% or less of B, where a matrix with restricted amount of 0.04% or less of P and 0.02% or less of S exhibits a ferrite single-phase texture.

[0008] Patent Literature 2 discloses a ferritic stainless steel that is excellent in crevice corrosion resistance, the ferritic stainless steel containing 0.001 to 0.02% of C, 0.001 to 0.02% of N, 0.01 to 0.3% of Si, 0.05 to 1% of Mn, 0.04% or less of P, 0.15 to 2% of Ni, 11 to 22% of Cr, 0.01 to 0.5% of Ti, and one or more of 0.5 to 3.0% of Mo, 0.02 to 0.6% of Nb and 0.1 to 1.5% of Cu in an amount satisfying $Cr + 3Mo + 6(Ni + Nb + Cu) \geq 22$. Both of Patent Literatures 1 and 2 relate to a stainless steel containing Ni to provide improved crevice corrosion resistance, where corrosion growth speed is restrained to enhance the pitting resistance. However, nothing is disclosed on the corrosion resistance when an oxide film is formed by heating.

[0009] Patent Literature 3 discloses a ferritic stainless steel containing 0.0010 to 0.30% of C, 0.0010 to 0.050% of N, 0.01 to 1.0% of Si, 0.01 to 1.0% of Mn, 0.04% or less of P, 0.010% or less of S, 1.0% or less of Ni, 10.0 to 30.0% of Cr, 0.010% or less of O, 0.005 to 0.10% of one or both of Sn and Sb, and, optionally, 0.0050 to 0.5% of Ti and/or 0.01 to 1.0% of Nb as necessary. The presence of one or both of Sn and Sb prevents grain boundary segregation of P to restrain surface flaws caused due to intergranular corrosion during sulfuric acid pickling.

[0010] Patent Literature 4 discloses a manufacturing method of a steel plate containing high-purity Cr that is excellent in pressing formability, the steel plate containing 0.02% or less of C, 0.02% or less of N, 3 to 30% of Cr, and one or both of Ti and Nb in an amount satisfying $(Ti + Nb) / (C + N) \geq 8$, where a ferrite particle diameter of a cast product and a winding temperature during a hot rolling step are defined in predetermined ranges. It is also disclosed that 0.5% or less of Sn content is effective in order to restrain intergranular corrosion caused by Cr carbonitride.

[0011] Patent Literature 5 discloses a ferritic stainless steel that is excellent in crevice corrosion resistance, the ferritic stainless steel containing 0.001 to 0.02% of C, 0.001 to 0.02% of N, 0.01 to 0.5% of Si, 0.05 to 1% of Mn, 0.04% or less of P, 0.01% or less of S, 12 to 25% of Cr, one or both of 0.02 to 0.5% of Ti and 0.02 to 1% of Nb, and one or both of 0.005 to 2% of Sn and 0.005 to 1% of Sb. Similarly to Ni in Patent Literatures 1 and 2, Patent Literature 5 relates to a

stainless steel containing Sn and/or Sb to provide improved crevice corrosion resistance, where corrosion growth rate is inhibited to enhance the pitting resistance. However, nothing is disclosed in Patent Literatures 3 to 5 on the corrosion resistance under the circumstances that an oxide film is formed by heating.

[0012] Patent Literature 6 discloses an alloy-saving ferritic stainless steel for an automobile exhaust system component that is excellent in corrosion resistance after heating, the ferritic stainless steel containing 0.015% or less of C, 0.015% or less of N, 0.10 to 0.50% of Si, 0.05 to 0.50% of Mn, 0.050% or less of P, 0.0100% or less of S, 10.5 to 16.5% of Cr, one or both of 0.03 to 0.30% of Ti and 0.03 to 0.30% of Nb, and one or both of 0.03 to 0.50% of Sn and 0.03 to 0.50% of Sb in an amount satisfying $Cr + Si + 0.5Mn + 10Al + 15(Sn + Sb) \geq 13$.

[0013] Patent Literature 7 discloses an Mo-saving ferritic stainless steel for an automobile exhaust system component that is excellent in corrosion resistance after heating, the ferritic stainless steel containing 0.015% or less of C, 0.015% or less of N, 0.01 to 0.50% of Si, 0.01 to 0.50% of Mn, 0.050% or less of P, 0.010% or less of S, 16.5 to 22.5% of Cr, 0.01 to 0.100% of Al, one or both of 0.03 to 0.30% of Ti and 0.03 to 0.30% of Nb, and one or both of 0.03 to 1.00% of Sn and 0.05 to 1.00% of Sb.

[0014] Patent Literature 8 discloses a ferritic stainless steel for an automobile exhaust system component, the ferritic stainless steel containing 0.015% or less of C, 0.015% or less of N, 0.01 to 0.50% of Si, 0.01 to 0.50% of Mn, 0.050% or less of P, 0.010% or less of S, 0.5 to 2.0% of Ni, 16.5 to 22.5% of Cr, 0.010 to 0.100% of Al, 0.01 to 0.50% of Sn, and one or both of 0.03 to 0.30% of Ti and 0.03 to 0.30% of Nb. All of Patent Literatures 6 to 8 disclose corrosion resistance under the circumstances that an oxide film is formed by heating. However, the composition and formation conditions of the oxide film are not mentioned in Patent Literatures 6 to 8.

CITATION LIST

PATENT LITERATURE(S)

[0015]

Patent Literature 1 JP 2005-89828 A
 Patent Literature 2 JP 2006-257544 A
 Patent Literature 3 JP 11-92872 A
 Patent Literature 4 JP 2002-38221 A
 Patent Literature 5 JP 2008-190003 A
 Patent Literature 6 JP 2010-31315 A
 Patent Literature 7 JP 2010-116619 A
 Patent Literature 8 JP 2011-190504 A

SUMMARY OF THE INVENTION

PROBLEM(S) TO BE SOLVED BY THE INVENTION

[0016] Thickness and weight reduction and increase in lifetime are demanded of exhaust system components for an automobile, a motor cycle, a commercial vehicle, a construction machine and the like. Improvement in corrosion resistance is further required of downstream exhaust system components. An oxide film is locally formed on the components in practical use due to heat applied during welding for assembly and travelling. The formed oxide film is inferior in corrosion resistance as compared with a material without the oxide film, and thus the pitting corrosion lifetime and rust resistance are greatly influenced by the presence of the oxide film. Accordingly, an improvement in corrosion resistance with the oxide film being formed is effective for reducing the thickness, increasing the lifetime and maintaining the good appearance of the component.

[0017] The invention has been achieved in view of the above problems. An object of the invention is to provide a ferritic stainless steel excellent in corrosion resistance after heating and suitably usable as a material for an exhaust system component, an exhaust system component, and a manufacturing method of the ferritic stainless steel and the exhaust system component.

MEANS FOR SOLVING THE PROBLEM(S)

[0018] A summary of some of aspects of the invention capable of achieving the above object is as follows.

(1) A ferritic stainless steel for exhaust system components excellent in corrosion resistance after heating, the ferritic stainless steel including: 0.015 mass% or less of C; 0.02 mass% or less of N; 0.03 mass% to 1.0 mass% of Si; 1.0

mass% or less of Mn; 0.04 mass% or less of P; 0.01 mass% or less of S; 10.5 mass% to 22.5 mass% of Cr; 0.02 mass% to 0.5 mass% of Sn; 0.003 mass% to 0.2 mass% of Al; one or both of 0.03 mass% to 0.35 mass% of Ti and 0.03 mass% to 0.6 mass% of Nb; and a remnant including Fe and inevitable impurities, in which a grain size number on a surface of the ferritic stainless steel is 6 or more, and 2 to 15 nm of a layer containing Sn at a concentration twice or more of a Sn concentration in a base material is formed on the ferritic stainless steel when the ferritic stainless steel is heated in the atmosphere under a condition satisfying a formula (I),

$$\exp(-23000 / T) \times t \geq 4.3 \times 10^{-15} \dots(I)$$

where T represents a temperature (K) and t represents a time (s).

(2) A ferritic stainless steel for exhaust system components excellent in corrosion resistance after heating, the ferritic stainless steel including: 0.015 mass% or less of C; 0.02 mass% or less of N; 0.03 mass% to 1.0 mass% of Si; 1.0 mass% or less of Mn; 0.04 mass% or less of P; 0.01 mass% or less of S; 10.5 mass% to 22.5 mass% of Cr; 0.02 mass% to 0.5 mass% of Sn; 0.003 mass% to 0.2 mass% of Al; one or both of 0.03 mass% to 0.35 mass% of Ti and 0.03 mass% to 0.6 mass% of Nb; and a remnant including Fe and inevitable impurities, in which a grain size number on a surface of the ferritic stainless steel is 6 or more, and 2 to 15 nm of a layer containing Sn at a concentration twice or more of a Sn concentration in a base material is formed on the ferritic stainless steel.

(3) The ferritic stainless steel for exhaust system component excellent in corrosion resistance after heating according to the above aspects of the invention, further including at least one of first group and a second group, the first group consisting of one or more of 0.05 mass% to 1.5 mass% of Cu, 0.1 mass% to 1.2 mass% of Ni, 0.03 mass% to 3 mass% of Mo, 0.03 mass% to 1 mass% of W, 0.05 mass% to 0.5 mass% of V and 0.01 mass% to 0.5 mass% of Sb, the second group consisting of one or more of 0.03 mass% to 0.5 mass% of Zr, 0.02 mass% to 0.2 mass% of Co, 0.0002 mass% to 0.002 mass% of Ca, 0.0002 mass% to 0.002 mass% of Mg, 0.0002 mass% to 0.005 mass% of B, 0.001 mass% to 0.01 mass% of REM, 0.0002 mass% to 0.01 mass% of Ga and 0.01 mass% to 0.5 mass% of Ta.

(4) The ferritic stainless steel for exhaust system components excellent in corrosion resistance after heating according to any one of the above aspects of the invention, in which the Sn content is 0.02 mass% or more and less than 0.05 mass% and/or 0.07 mass% or more and 0.3 mass% or less.

(5) The ferritic stainless steel for exhaust system components excellent in corrosion resistance after heating according to any one of the above aspects of the invention, in which the Ni content is 0.1 mass% or more and less than 0.5 mass%.

(6) An exhaust system component excellent in corrosion resistance after heating, the exhaust system component being made from a ferritic stainless steel, the ferritic stainless steel including: 0.015 mass% or less of C; 0.02 mass% or less of N; 0.03 mass% to 1.0 mass% of Si; 1.0 mass% or less of Mn; 0.04 mass% or less of P; 0.01 mass% or less of S; 10.5 mass% to 22.5 mass% of Cr; 0.02 mass% to 0.5 mass% of Sn; 0.003 mass% to 0.2 mass% of Al; one or both of 0.03 mass% to 0.35 mass% of Ti and 0.03 mass% to 0.6 mass% of Nb; and a remnant including Fe and inevitable impurities, in which a grain size number on a surface of the ferritic stainless steel is 6 or more, and 2 to 15 nm of a layer containing Sn at a concentration twice or more of a Sn concentration in a base material is formed on the ferritic stainless steel.

(7) The exhaust system component excellent in corrosion resistance after heating and being made from the ferritic stainless steel according to the above aspect of the invention, in which the ferritic stainless steel further includes at least one of a first group and a second group, the first group consisting of one or more of 0.05 mass% to 1.5 mass% of Cu, 0.1 mass% to 1.2 mass% of Ni, 0.03 mass% to 3 mass% of Mo, 0.03 mass% to 1 mass% of W, 0.05 mass% to 0.5 mass% of V and 0.01 mass% to 0.5 mass% of Sb, the second group consisting of one or more of 0.03 mass% to 0.5 mass% of Zr, 0.02 mass% to 0.2 mass% of Co, 0.0002 mass% to 0.002 mass% of Ca, 0.0002 mass% to 0.002 mass% of Mg, 0.0002 mass% to 0.005 mass% of B, 0.001 mass% to 0.01 mass% of REM, 0.0002 mass% to 0.01 mass% of Ga and 0.01 mass% to 0.5 mass% of Ta.

(8) The exhaust system component excellent in corrosion resistance after heating and being made from the ferritic stainless steel according to any one of the above aspects of the invention, in which the Sn content is 0.02 mass% or more and less than 0.05 mass% and/or 0.07 mass% or more and 0.3 mass% or less.

(9) The exhaust system component excellent in corrosion resistance after heating and being made from the ferritic stainless steel according to any one of the above aspects of the invention, in which the Ni content is 0.1 mass% or more and less than 0.5 mass%.

(10) A manufacturing method of the ferritic stainless steel for exhaust system components excellent in corrosion resistance after heating according to any one of the above aspects of the invention, in which, when the ferritic stainless steel according to any one of the above aspects of the invention is manufactured, a finish annealing temperature in a cold rolling step is 1030 degrees C or less, and when the ferritic stainless steel is cooled from a

cold-rolled-sheet annealing temperature, a cooling rate in a temperature range from 800 to 600 degrees C is less than 20 degrees C/s.

(11) A manufacturing method of the ferritic stainless steel for exhaust system components excellent in corrosion resistance after heating according to any one of the above aspects of the invention, in which when the ferritic stainless steel according to any one of the above aspects of the invention is manufactured, a finish annealing temperature in a cold rolling step is 1030 degrees C or less, and when the ferritic stainless steel is cooled from a cold-rolled-sheet annealing temperature, a cooling rate in a temperature range from 800 to 600 degrees C is less than 5 degrees C/s.

(12) A manufacturing method of the exhaust system component excellent in corrosion resistance after heating and being made from the ferritic stainless steel according to any one of the above aspects of the invention, in which, when the ferritic stainless steel forming the exhaust system component according to any one of the above aspects of the invention is manufactured, a finish annealing temperature in a cold rolling step is 1030 degrees C or less, and when the ferritic stainless steel is cooled from a cold-rolled-sheet annealing temperature, a cooling rate in a temperature range from 800 to 600 degrees C is less than 20 degrees C/s.

(13) A manufacturing method of the exhaust system component excellent in corrosion resistance after heating and being made from the ferritic stainless steel according to any one of the above aspects of the invention, in which when the ferritic stainless steel forming the exhaust system component according to any one of the above aspects of the invention is manufactured, a finish annealing temperature in a cold rolling step is 1030 degrees C or less, and when the ferritic stainless steel is cooled from a cold-rolled-sheet annealing temperature, a cooling rate in a temperature range from 800 to 600 degrees C is less than 5 degrees C/s.

[0019] The ferritic stainless steel of the above aspects of the invention is suitable for a material of exhaust system components of an automobile, a motor cycle, a commercial vehicle, a construction machine and the like. Since the ferritic stainless steel of the above aspects of the invention improves the corrosion resistance of a portion including a welded portion that is subjected to heating in use, the ferritic stainless steel contributes to an increase in lifetime of the exhaust system component and thickness and weight reduction of the exhaust system component.

BRIEF DESCRIPTION OF DRAWING(S)

[0020] Fig. 1 shows an influence of Sn content exerted on a maximum pit depth.

DESCRIPTION OF EMBODIMENT(S)

[0021] Exemplary embodiment(s) of the invention will be described below in detail.

[0022] In studying corrosion resistance after heating, the inventors of the invention focused on an oxide film formed by the heating and conducted detailed studies. This is because the inventors suspected that the deterioration in corrosion resistance due to heating was primarily dependent on a formation status of the oxide film.

[0023] When a ferritic stainless steel is heated at 573 to 1073 K in the atmosphere, an oxide film having Fe-rich external layer and Cr-rich internal layer is formed on the surface of the ferritic stainless steel. The oxide film is inferior to a passivation film of unheated stainless steel in terms of performance for shielding a material from a corrosive environment. Accordingly, with an identical chemical composition of the material, the heated material is inferior in corrosion resistance. Thus, it is believed that an improvement in the formation status of the oxide film would lead to an improvement in corrosion resistance after heating. However, since the ferritic stainless steel is mostly formed of Fe and Cr, it is inevitable that the oxide film is primarily formed of these two elements. Accordingly, a use of a third element other than Fe and Cr is attempted.

[0024] When steel is heated at a temperature ranging from 573 to 1073 K approximately for 24 hours at the maximum, though an oxide film made primarily of the primary elements (i.e. Fe and Cr) having a thickness of approximately 20 nm to sub-microns is formed, it is difficult to concentrate minute amounts of metal element(s) added in the steel in the entirety of the oxide film. Accordingly, it was attempted to concentrate the element(s) effective for improving corrosion resistance at and near the border between the oxide film and a base material. If the element(s) is less likely to be oxidized than Fe and Cr, the element(s) can be concentrated in a metal form in an environment in which Fe and Cr are oxidized (e.g. in the atmosphere). In view of the above, Cu, Ni and Sn are studied as the above elements in terms of corrosion resistance.

[0025] When oxide films formed after heating in the atmosphere on ferritic stainless steels each added with Cu alone, Ni alone and Sn alone were compared, it was found that the element most likely to concentrate at the border between the oxide film and the base material among the three elements was Sn. As a result of chemical status analysis using an X-ray photoelectric spectroscopy (referred to as XPS hereinafter), it was found that Sn was concentrated in a metal form.

[0026] Then, ferritic stainless steel sheets containing 0.004C-0.008N-0.1Si-0.1Mn-16.5Cr-0.2Nb-0.1Ti-0.03Al system (the numbers representing contents of individual elements (mass%)) as a base component and Sn content ranging from

0 to 0.5 mass% were prepared as samples, and each of the samples was subjected to a heat treatment in the atmosphere at 673 K for 24 hours and, subsequently, was subjected to two cyclic corrosion tests. It should be noted that, when the steel sheets were cooled from a finish annealing temperature during the production of the steel sheet, the cooling rate of the steel sheets was 15 degrees C/s in a temperature range from 800 to 600 degrees C. Grain size on a Z-surface of the steel plates was 6.5.

[0027] In the first one of the cyclic corrosion tests, which is intended to assess pitting corrosion resistance, one cycle of: spraying 5% NaCl solution at 35 degrees C for two hours; drying at 60 degrees C for four hours; and wetting at 50 degrees C for two hours in accordance with JASO M609-91 was repeated for 120 times (i.e. 120 cycles). After completion of the test, corrosion product was removed using di-ammonium hydrogen citrate aqueous solution. Subsequently, a maximum pit depth was measured using a microscope focal depth method. In the second one of the cyclic corrosion tests, which is intended to assess rust resistance, one cycle of: spraying ten-fold diluted artificial seawater at 35 degrees C for four hours; drying at 60 degrees C for two hours; and wetting at 50 degrees C for two hours was repeated for three times (i.e. three cycles). After completion of the test, rust generation level was graded using a rating number (abbreviated as RN hereinafter) according to JIS G0595. It should be noted that a larger number of RN represents a more excellent rust resistance.

[0028] Fig. 1 shows an influence of the Sn content on the maximum pit depth measured in the first test. As shown in Fig. 1, it is understood that the presence of 0.02 mass% or more of Sn clearly reduces the maximum pit depth and the maximum pit depth is reduced in accordance with an increase in the Sn content. On the other hand, though RN rated in the second test was 5 when the Sn content was 0.001%, RN was 6 or more when 0.02 mass% or more of Sn was contained (i.e. the rust generation level was improved). The presence of rust is easily observable and degradation of appearance is clearly recognizable when RN is 5. Accordingly, the steel is judged inferior in quality when RN is 5 or less whereas the steel is judged excellent when RN is 6 or more. As described above, it is demonstrated that the presence of 0.02 mass% or more of Sn can improve the rust resistance in addition to the pitting corrosion resistance.

[0029] A sample containing 0.021 mass% of Sn was subjected to the same heat treatment as that in the above corrosion test and was examined using the XPS. It was found that an approximately 40-nm-thick oxide film having an Fe-rich external layer and a Cr-rich internal layer was formed on a surface of the sample and 0.02 to 0.04 at% in cation fraction of Sn was present in a region of approximately 2 nm at and near the border between the oxide film and the base material. The Sn content at and near the border between the oxide film and the base material increases in accordance with an increase in the Sn content in the sample. When 0.5 mass% of Sn was contained in the sample, 0.47 to 0.7 at% in cation fraction of Sn was detected over a region of approximately 10 nm. Since the Sn amount in the base material containing 0.5 mass% of Sn is approximately 0.22 at%, it is clear that Sn is concentrated at and near the border between the oxide film and the base material. In the invention, a layer present at and near the border between the oxide film and the base material and containing Sn at a larger concentration than the Sn content in the base material will be referred to as an Sn-concentrated layer hereinafter. It is found that, when the thickness of the Sn-concentrated layer is 2 nm or more and the Sn concentration in the Sn-concentrated layer is twice or more of the Sn content in the base material, the effect for improving the corrosion resistance of the invention can be exhibited.

[0030] The Sn content and thickness of the Sn-concentrated layer increase in accordance with an increase in heating temperature and heating time. However, excessive heating results in an uneven growth of the oxide film and, consequently, uneven thickness of the Sn-concentrated layer, and also results in saturation of corrosion resistance improving effect. With the maximum heating temperature and time (i.e. at 1073 K for 24 hours), the thickness of the Sn-concentrated layer was approximately 15 nm.

[0031] Though the reason why the concentration of Sn at and near the border between the oxide film and the base material effectively reduces the pit depth in the cyclic corrosion test and improves the rust resistance is not fully understood, it is speculated that this is because dissolved and ionized Sn serves as an inhibitor (i.e. a corrosion inhibitor).. The progress speed of the pitting corrosion is thus reduced to decrease the pit depth and growth of lately generated small pit is stopped, thereby improving the rust resistance. It is believed that, since the Sn is present in a metal form at and near the border between the oxide film and the base material at a higher concentration than in the base material, the corrosion of the base material can be more effectively restrained.

[0032] In order to concentrate Sn at and near the border between the oxide film and the base material, it is preferable that heating is performed in the atmosphere so that the following formula (I) is satisfied.

$$\exp(-23000 / T) \times t \geq 4.3 \times 10^{-15} \dots(I)$$

T: temperature (K), t: time (s)

A preferable value for the right side of the formula (I) is 8.6×10^{-15} . On the other hand, since excessive heating results

in saturation of the concentration of Sn, the upper limit of the value represented by the left side of the formula (I) is preferably 4.5×10^{-9} .

[0033] Further, though Fe and Cr are oxidized by heating to promote the concentration of Sn at and near the border between the oxide film and the base material, it is necessary that a grain size number on the surface is 6 or more in order to reach the Sn concentration required in the invention. Grain boundary diffusion dominantly occurs in the temperature range of 573 to 1073 K. Accordingly, with a small grain size, the diffusion of Sn is promoted to progress the concentration of Sn. Preferably, the grain size number is 6.5 or more and, more preferably, 7 or more. In addition, it is effective to form a processed layer on the surface by polishing and the like in order to concentrate Sn.

[0034] The effects of each of alloy elements of the invention and the reason for the specified content thereof will be detailed below. In the following, % refers to mass% except otherwise defined.

C: 0.015% Or Less

[0035] Since C decreases intergranular corrosion resistance and formability, the content of C should be kept at a low level. Accordingly, the upper limit of the C content is set at 0.015%, preferably at 0.012%. However, when the C content is excessively low, a necessary strength cannot be obtained and refining cost increases. Accordingly, the lower limit of the C content is preferably set at 0.002%, more preferably at 0.003%.

N: 0.02% Or Less

[0036] Though N is an element effective for improving pitting resistance, since N decreases intergranular corrosion resistance and formability, the content of N should be kept at a low level. Accordingly, the upper limit of the N content is set at 0.02%, preferably at 0.018%. However, when the N content is excessively low, necessary strength cannot be obtained and refining cost increases. Accordingly, the lower limit of the N content is preferably set at 0.002%, more preferably at 0.003%.

Si: 0.03% Or More And 1.0% Or Less

[0037] Since Si is an element effective for improvement in oxidation resistance and adapted to improve the corrosion resistance after heating, it is necessary that Si content is 0.03% or more. The lower limit of Si content is preferably 0.05%, more preferably 0.1%, further preferably 0.2%. However, since the addition of excessive amount of Si results in decrease in formability, the upper limit of Si content is set at 1.0%. The upper limit of Si content is preferably 0.8%, more preferably 0.6%, further preferably 0.5%.

Mn: 1.0% Or Less

[0038] Since Mn deteriorates corrosion resistance, the content of Mn has to be limited. Accordingly, the upper limit of the Mn content is set at 1.0%, preferably at 0.5%. However, extremely lowering the Mn content results in an increase in the production cost. Accordingly, the lower limit of the Mn content is preferably set at 0.03%, more preferably at 0.05%.

P: 0.04% Or Less

[0039] Since P deteriorates formability and weldability, the content of P has to be limited. Accordingly, the upper limit of the P content is set at 0.04%. However, extremely lowering the P content results in an increase in the production cost. Accordingly, the upper limit of the P content is preferably set at 0.02%.

S: 0.01% Or Less

[0040] Since S deteriorates corrosion resistance, the content of S has to be limited. Accordingly, the upper limit of the S content is set at 0.01%, preferably at 0.005%, more preferably at 0.002%.

Cr: 10.5% or more and 22.5% Or Less

[0041] Since Cr is a basic element for ensuring the corrosion resistance, the lower limit of Cr content has to be set at 10.5%. Preferably, the Cr content is 11.0% or more, more preferably 12.5% or more, further preferably 14.0% or more. On the other hand, though the corrosion resistance can be improved in accordance with increase in the Cr content, excessive addition of Cr leads to deterioration in formability and productivity. Accordingly, the Cr content is 22.5% or less, preferably 20.5% or less, further preferably 19.5% or less, further more preferably 18.0% or less.

Sn: 0.02% or more and 0.5% Or Less

[0042] Sn is an element extremely useful for improving the corrosion resistance after heating, and is the most important in the invention. Accordingly, the lower limit of the Sn content is set at 0.02%, preferably at 0.05%, more preferably at 0.07% and further preferably at 0.1%. On the other hand, though the corrosion resistance after heating can be improved in accordance with an increase in the Sn content, excessive addition of Sn leads to deterioration in formability and productivity. Accordingly, the Sn content is 0.5% or less, preferably 0.4% or less, further preferably 0.3% or less, further more preferably 0.25% or less. In addition, it is preferable to adjust the Sn content depending on the required level of the corrosion resistance after heating. Specifically, when the required level of the corrosion resistance after heating is low, the Cr content is suitably defined to be 0.02% or more and less than 0.05%. When a normal level of the corrosion resistance after heating is required, the Cr content is suitably defined to be 0.07% or more and 0.3% or less. When the required level of the corrosion resistance after heating is high, the Cr content is suitably defined to be 0.3% or more and 0.5% or less. It is more preferable that the Cr content is 0.1% or less when the normal level of the corrosion resistance after heating is required.

Al: 0.003% Or More And 0.2% Or Less

[0043] Al is effective as a deoxidizing element and it is necessary that 0.003% or more of Al is contained. Al content is preferably 0.005% or more, more preferably 0.01%. However, since the addition of excessive amount of Al results in deterioration in toughness and productivity, the upper limit of Al content is set at 0.2%. The upper limit of Al content is preferably 0.15%, more preferably 0.1%.

[0044] The stainless steel of the exemplary embodiment contains one or both of Ti and Nb in the following amount.

Ti: 0.03% Or More And 0.35% Or Less

[0045] Ti is an element that is fixed with C and N to form a Ti carbonitride to inhibit intergranular corrosion. Further, Ti is also fixed with S to form a Ti sulfide or Ti carbon-sulfide to improve the corrosion resistance. Accordingly, the lower limit of the Ti content is set at 0.03%, preferably at 0.05%, more preferably at 0.07%. However, since the addition of excessive amount of Ti results in an adverse effect in terms of formability and productivity, the upper limit of Ti content is set at 0.35%. The upper limit of the Ti content is preferably 0.32%, more preferably 0.28%. It should be noted that the Ti content should be $4(C + N) + 3S$ or more.

Nb: 0.03% Or More And 0.6% Or Less

[0046] Similarly to Ti, Nb is an element that is fixed with C and N to form an Nb carbonitride to inhibit the intergranular corrosion. In addition, Nb acts to improve high-temperature strength. Accordingly, the lower limit of the Nb content is set at 0.03%, preferably at 0.1%, more preferably at 0.2%. However, since the addition of excessive amount of Nb results in an adverse effect in terms of formability, the upper limit of Nb content is set at 0.6%. The upper limit of Nb content is preferably 0.55%, more preferably 0.5%.

[0047] The stainless steel of the exemplary embodiment may optionally further contain, in mass%, one or more of 0.05 to 1.5% of Cu, 0.1 to 1.2% of Ni, 0.03 to 3% of Mo, 0.03 to 1% of W, 0.05 to 0.5% of V, and 0.01 to 0.5% of Sb.

Cu: 0.05% Or More And 1.5% Or Less

[0048] Cu is an element that enhances corrosion resistance and strength. Accordingly, 0.05% or more of Cu may be added as necessary. The Cu content is preferably 0.2% or more, more preferably 0.3% or more. However, since the addition of excessive amount of Cu results in decrease in formability, the upper limit of Cu content is preferably set at 1.5% or less. The Cu content is more preferably 1.0% or less and further preferably 0.8% or less.

Ni: 0.1 % Or More And 1.2% Or Less

[0049] Ni is an element that enhances corrosion resistance. Accordingly, 0.1% or more of Ni may be added as necessary. Ni content is preferably 0.2% or more, more preferably 0.3% or more. However, excessive addition of Ni, which is expensive, results in deterioration in formability and in an increase in the production cost. Accordingly, the Ni content is preferably 1.2% or less, more preferably 0.9% or less and further preferably less than 0.5%.

Mo: 0.03% Or More And 3% Or Less

[0050] Mo is an element that enhances corrosion resistance and strength. Accordingly, 0.03% or more of Mo may be added as necessary. Preferably, the Mo content is 0.1 % or more, more preferably 0.3% or more, further preferably 0.7% or more. However, excessive addition of Mo results in deterioration in formability and, since Mo is expensive, increase in the production cost. Accordingly, the Mo content is preferably 3% or less, more preferably 2.2% or less and further preferably 1.8% or less.

W: 0.03% Or More And 1% Or Less

[0051] W is an element that enhances corrosion resistance. Accordingly, 0.03% or more of W may be added as necessary. The W content is preferably 0.2% or more, more preferably 0.5% or more. However, excessive addition of W, which is expensive, results in deterioration in formability, and in an increase in the production cost. Accordingly, the W content is preferably 1% or less, more preferably 0.8% or less.

V: 0.05% Or More And 0.5% Or Less

[0052] V is an element that enhances corrosion resistance. Accordingly, 0.05% or more of V may be added as necessary. The V content is further preferably 0.1% or more. However, excessive addition of V, which is expensive, results in deterioration in formability and in an increase in the production cost. Accordingly, the V content is preferably 0.5% or less, more preferably 0.3% or less.

Sb: 0.01% Or More And 0.5% Or Less

[0053] Sb is an element that enhances corrosion resistance. Accordingly, 0.01% or more of Sb may be added as necessary. The Sb content is preferably 0.03% or more, more preferably 0.05% or more. However, excessive addition of Sb results in deterioration in formability and productivity. Accordingly, the Sb content is preferably 0.5% or less, more preferably 0.3% or less.

[0054] The stainless steel of the exemplary embodiment may optionally further contain, in mass%, one or more of 0.03 to 0.5% of Zr, 0.02 to 0.2% of Co, 0.0002 to 0.002% of Ca, 0.0002 to 0.002% of Mg, 0.0002 to 0.005% of B, 0.001 to 0.01% of REM, 0.0002 to 0.01% of Ga, and 0.01 to 0.5% of Ta.

Zr: 0.03% Or More And 0.5% Or Less

[0055] Zr is an element that enhances corrosion resistance, especially intergranular corrosion resistance. Accordingly, 0.03% or more of Zr may be added as necessary. The Zr content is preferably 0.05% or more, more preferably 0.1% or more. However, excessive addition of Zr results in deterioration in formability and, since Zr is expensive, increase in the production cost. Accordingly, the Zr content is preferably 0.5% or less, more preferably 0.3% or less.

Co: 0.02% Or More And 0.2% Or Less

[0056] Co is an element that enhances secondary formability and toughness. Accordingly, 0.02% or more of Co may be added as necessary. The Co content is preferably 0.05% or more, more preferably 0.08% or more. However, excessive addition of Co results in an increase in the production cost. Accordingly, the Co content is preferably 0.2% or less, more preferably 0.18% or less.

Ca: 0.0002% Or More And 0.002% Or Less

[0057] Ca is an element that has deoxidization effect and the like and thus is useful in a refining process. Accordingly, 0.0002% or more of Ca may be added as necessary. The Ca content is more preferably 0.0004% or more. However, since Ca forms Ca sulfide to deteriorate the corrosion resistance, the Ca content is preferably 0.002% or less and more preferably 0.0015% or less.

Mg: 0.0002% Or More And 0.002% Or Less

[0058] Mg is an element that has deoxidization effect and the like and thus is useful in a refining process. In addition, Mg miniaturizes the texture to improve formability and toughness. Accordingly, 0.0002% or more of Mg may be contained, and more preferably 0.0005% or more of Mg may be contained as necessary. However, since excessive addition of Mg

deteriorates the corrosion resistance, the Mg content is preferably 0.002% or less and more preferably 0.0015% or less.

B: 0.0002% Or More And 0.005% Or Less

5 **[0059]** B is an element that enhances formability, especially secondary formability. Accordingly, 0.0002% or more of B may be added as necessary. The B content is more preferably 0.0003% or more. However, since excessive addition of B deteriorates intergranular corrosion resistance, the B content is preferably 0.005% or less and more preferably 0.002% or less.

10 REM: 0.001% Or More And 0.01% Or Less

[0060] REM represents a group of elements including La, Y, Ce, Pr, Nd and the like belonging to atomic numbers of 57-71. REM is a group of elements that have deoxidization effect and the like and thus is useful in a refining process. Accordingly, 0.001 % or more of REM may be added as necessary. However, excessive addition of REM results in an increase in the production cost. Accordingly, the REM content is preferably 0.01% or less.

Ga: 0.0002% Or More And 0.01% Or Less

20 **[0061]** Ga is an element that forms a stable sulfide to improve corrosion resistance and hydrogen embrittlement resistance. Accordingly, 0.0002% or more of Ga may be added as necessary. However, excessive addition of Ga results in an increase in the production cost. Accordingly, the Ga content is preferably 0.01% or less.

Ta: 0.01 % Or More And 0.5% Or Less

25 **[0062]** Ta is an element that enhances the corrosion resistance. Accordingly, 0.01% or more of Ta may be added as necessary. The Ta content is preferably 0.05% or more, more preferably 0.1% or more. However, excessive addition of Ta results in decrease in toughness and increase in the production cost. Accordingly, the Ta content is preferably 0.5% or less, more preferably 0.4% or less.

30 **[0063]** The stainless steel of the exemplary embodiment is basically manufactured according to a method typically employed in order to manufacture ferritic stainless steel. For instance, molten steel having the above chemical composition may be produced in a converter furnace or an electric furnace, refined in an AOD furnace or a VOD furnace, and formed into a steel piece through a continuous casting process or ingot-making process. The steel piece is then sequentially subjected to hot rolling, hot-rolled sheet annealing, pickling, cold rolling-finish annealing, and pickling. The hot-rolled sheet annealing may be omitted and/or the sequence of cold rolling, finish annealing and pickling may be repeated as necessary. A use of a small-diameter roller having a diameter of 150 mm or less in the cold rolling step is effective for concentrating Sn at and near the border between the oxide film and the base material. Further, in order to promote recrystallization, the finish annealing temperature is preferably 800 degrees C or more and, in order to restrain the grains from being coarsened, the finish annealing temperature is preferably 1030 degrees C or less. Further, in order to enhance grain boundary segregation of Sn and to promote the concentration of Sn at and near the border between the oxide film and the base material, it is preferable that the cooling rate in a temperature range from 800 to 600 degrees C during cooling from the finish annealing temperature is less than 20 degrees C/s on average. More preferably, the cooling rate is less than 15 degrees C/s on average, more preferably less than 5 degrees C/s on average.

35 **[0064]** To produce a ferritic stainless steel sheet containing the above components of the exemplary embodiment, the finish annealing temperature of the cold rolling is set at an appropriate temperature of 1030 degrees C or less and the cooling rate in a temperature range from 800 to 600 degrees C during cooling from the finish annealing temperature is less than 20 degrees C/s on average, so that the grain size number on the surface of the steel becomes 6 or more. Accordingly, when the ferritic stainless steel sheet is heated in the atmosphere under the condition satisfying the formula (I), 2 to 15 nm of the layer containing Sn at a concentration twice or more of the Sn content in the base material can be formed.

50 **[0065]** Further, when a ferritic stainless steel sheet containing the above components of the exemplary embodiment is to be produced, the finish annealing temperature of the cold rolling is set at an appropriate temperature of 1030 degrees C or less, the cooling rate in a temperature range from 800 to 600 degrees C during cooling from the finish annealing temperature is less than 20 degrees C/s on average and the steel sheet is heated in the atmosphere under the condition satisfying the formula (1), so that a ferritic stainless steel sheet whose grain size number on the surface is 6 or more and having 2 to 15 nm of a layer containing Sn at a concentration twice or more of the Sn content in the base material can be manufactured.

[0066] The heating in the atmosphere under the condition satisfying the formula (I) corresponds to the heating applied on the exhaust system component when a vehicle travels. The heating in the atmosphere under the condition satisfying

the formula (I) may be applied on a steel sheet before being assembled into the exhaust system component.

[0067] The exhaust system component excellent in corrosion resistance after heating according to the exemplary embodiment is manufactured using the steel plate as a material according to a typical manufacturing method of a stainless steel pipe for exhaust system components such as electric resistance welding, TIG welding and laser welding. Examples

[0068] The invention will be described in more details with reference to Examples.

[0069] 1 mm-thick cold-rolled steel sheets were prepared by: melting stainless steel of the compositions shown in Table 1-1 in a 180 kg vacuum melting furnace; casting the stainless steel into steel ingots of 45 kg; and subjecting the steel ingots to a process including hot rolling, hot-rolled sheet annealing, shot blasting, cold rolling, and finish annealing. Each of the hot-rolled sheets was prepared by rolling each of the ingots of 50 mm thickness to a thickness of 5 mm at a heating temperature of 1200 degrees C and subsequently air-cooling the hot-rolled sheet. The hot-rolled sheet annealing was applied by air-cooling for one minute in a temperature range from 850 to 1050 degrees C. Subsequently, scales were removed by the shot blasting. Then, each of the steel sheets was cold-rolled to obtain a 1-mm-thick steel sheet and was subjected to the finish annealing in which the steel sheets were held for one minute under the temperatures shown in Table 1-2. Thereafter, the steel plates were cooled under the conditions shown in Table 1-2.

[0070] A specimen of 70 mm in width and 150 mm in length was cut out from each of the cold-rolled steel sheets. A test surface of the specimen was wet-polished up to #600 using Emery paper. Subsequently, the specimen was subjected to a heat treatment at 673 K in the atmosphere for 24 hours. The value represented by the left side of the formula (I) at this time is 1.2×10^{-10} . For comparison sake, Comparative Example 5 in Table 1-2 (steel 7) was subjected to a heat treatment at 523 K in the atmosphere for 15 minutes instead of the heat treatment at 673 K for 24 hours. The value represented by the left side of the formula (I) at this time is 7.1×10^{-17} .

[0071] The distribution of the Sn content at and near the surface of the steel sheet after the heat treatment was measured using an XPS. When the specimen used for the aforementioned cyclic corrosion test was subjected to the heat treatment, the sample for the surface analysis was simultaneously subjected to the heat treatment. The XPS was manufactured by ULVAC-PHI, Inc. having an X-ray source of mono-A1 K_{α} ray, where elemental analysis in the depth direction was performed using Ar-ion sputtering. The sputtering rate was 1.5 nm/min in terms of SiO_2 . The thickness of the Sn-concentrated layer present at the border region between the oxide film and the base material was measured (shown in Table 1-2). The thickness of the Sn-concentrated layer represents a thickness of the region in which detected Sn concentration was higher than the Sn content in the base material. The lowest Sn concentration in the Sn-concentrated layer is shown in Table 1-2 in atom%. A value obtained by dividing the Sn concentration in the Sn-concentrated layer by the Sn content in the base material is shown in Table 1-2 as "Concentration Degree."

[0072] The corrosion resistance was evaluated using the two types of cyclic corrosion tests. In the first one of the cyclic corrosion tests, one cycle of: spraying 5% NaCl solution at 35 degrees C for two hours; drying at 60 degrees C for four hours; and wetting at 50 degrees for two hours in accordance with JASO M609-91 was repeated for 120 times (i.e. 120 cycles). After completion of the cyclic corrosion test, corrosion product was removed using di-ammonium hydrogen citrate aqueous solution. Subsequently, a maximum pit depth was measured using a microscope focal depth method. In the second one of the cyclic corrosion tests, one cycle of: spraying ten-fold diluted artificial seawater at 35 degrees C for four hours; drying at 60 degrees C for two hours; and wetting at 50 degrees for two hours was repeated for three times (i.e. three cycles). After completion of the test, a rust generation level was graded using the rating number according to JIS G0595.

[0073] A specimen of 20 mm in width and 20 mm in length was cut out from the same cold-rolled steel sheet. A surface of the specimen was mirror-polished and subsequently etched to expose microstructure. A grain size on a Z-surface (a surface parallel to the surface) was measured in accordance with JIS G0551.

Table 1-1

		Chemical Composition (mass%)											Others
		C	N	Si	Mn	P	S	Cr	Sn	Ti	Nb	Al	
1	Steel 1	0.004	0.018	0.49	0.26	0.025	0.002	17.89	0.13	0.34	—	0.004	—
2	Steel 2	0.012	0.017	0.21	0.06	0.021	0.001	14.11	0.24	—	0.49	0.031	—
3	Steel 3	0.003	0.004	0.11	0.11	0.029	0.003	19.43	0.07	0.27	—	0.078	—
4	Steel 4	0.007	0.014	0.78	0.04	0.031	0.001	10.61	0.49	0.06	0.31	0.003	—
5	Steel 5	0.006	0.013	0.60	0.09	0.032	0.001	11.12	0.46	0.21	—	0.010	—
6	Steel 6	0.005	0.011	0.51	0.10	0.026	0.004	12.78	0.39	0.22	0.04	0.021	—
7	Steel 7	0.004	0.008	0.20	0.09	0.025	0.002	13.87	0.03	0.13	0.12	0.036	—
8	Steel 8	0.004	0.005	0.06	0.94	0.022	0.001	20.45	0.05	0.09	0.19	0.085	—
9	Steel 9	0.004	0.005	0.05	0.48	0.023	0.001	22.43	0.03	0.11	0.21	0.092	—
10	Steel 10	0.010	0.015	0.26	0.10	0.023	0.001	13.97	0.22	—	0.48	0.025	0.32Cu
11	Steel 11	0.009	0.014	0.31	0.14	0.025	0.001	14.52	0.19	0.31	—	0.029	0.38Ni
12	Steel 12	0.007	0.012	0.19	0.15	0.028	0.001	14.33	0.15	—	0.58	0.019	0.74Mo, 0.27Ni
13	Steel 13	0.005	0.015	0.45	0.31	0.028	0.003	18.12	0.11	0.25	—	0.008	0.10Sb, 0.0006B
14	Steel 14	0.003	0.013	0.46	0.30	0.024	0.002	17.45	0.09	—	0.38	0.013	0.11V, 0.82W, 0.06Zr, 0.0009Ca
15	Steel 15	0.007	0.010	0.44	0.29	0.024	0.004	17.12	0.18	0.23	—	0.041	0.09Co, 0.0006Mg, 0.005REM
16	Steel 16	0.006	0.009	0.92	0.35	0.025	0.001	13.26	0.04	0.11	0.19	0.020	0.15Ni, 0.29Cu, 0.11Ta
17	Steel 17	0.011	0.004	0.82	0.41	0.022	0.001	15.35	0.02	0.25	—	0.009	0.46Ni, 0.0004Ga
18	Steel 18	0.013	0.007	0.25	0.22	0.028	0.002	16.89	0.09	—	0.46	0.041	—
1	Steel 19	0.011	0.017	0.16	0.16	0.025	0.002	14.09	0.01	—	0.39	0.029	—
2	Steel 20	0.005	0.008	0.15	0.36	0.025	0.003	<u>10.47</u>	0.09	—	0.29	0.026	—
3	Steel 21	0.006	0.009	<u>0.02</u>	0.35	0.024	0.003	10.72	0.09	—	0.31	0.031	—
4	Steel 7	0.004	0.008	0.20	0.09	0.025	0.002	13.87	0.03	0.13	0.12	0.036	—
5	Steel 7	0.004	0.008	0.20	0.09	0.025	0.002	13.87	0.03	0.13	0.12	0.036	—
6	Steel 7	0.004	0.008	0.20	0.09	0.025	0.002	13.87	0.03	0.13	0.12	0.036	—

(Note) The underlined shows values outside the scope of the invention.

Table 1-2

		Finish annealing temperature (°C)	Cooling rate (°C/s) 800 to 600°C	Grain size number	Sn-concentrated layer			Maximum pit depth (μm)	RN
					Concentration degree	Thickness (nm)	Sn concentration (at%) *		
1	Steel 1	860	15	6.5	2.1	6	0.12	299	7
2	Steel 2	970	7	7.5	2.8	8	0.30	322	6
3	Steel 3	870	15	6.0	2.3	5	0.07	313	8
4	Steel 4	930	8	7.5	3.0	10	0.64	288	6
5	Steel 5	860	15	6.5	2.1	10	0.43	356	6
6	Steel 6	880	15	6.5	2.2	9	0.38	343	7
7	Steel 7	870	3	8.0	3.8	5	0.05	379	6
8	Steel 8	930	10	6.5	2.7	4	0.06	275	9
9	Steel 9	930	4	7.0	3.8	2	0.05	269	9
10	Steel 10	980	10	7.0	2.6	4	0.25	331	6
11	Steel 11	880	15	6.0	2.3	6	0.19	296	7
12	Steel 12	1000	4	8.0	3.5	5	0.23	157	8
13	Steel 13	860	15	6.5	2.3	4	0.11	265	7
14	Steel 14	960	10	7.5	3.0	6	0.12	245	6
15	Steel 15	860	15	6.5	2.3	8	0.18	277	7
16	Steel 16	870	10	6.5	2.3	4	0.04	391	6
17	Steel 17	880	10	6.5	2.3	3	0.02	386	6
18	Steel 18	990	15	7.0	2.3	5	0.09	361	6
1	Steel 19	950	10	6.5	2.3	2	0.01	645	5
2	Steel 20	940	15	6.0	2.8	5	0.11	575	4
3	Steel 21	930	15	6.0	2.5	5	0.10	559	4
4	Steel 7	1035	15	4.0	1.5	3	0.02	452	5
5	Steel 7	890	15	6.5	<u>0.8</u>	-	0.01	532	5
6	Steel 7	890	<u>30</u>	6.5	<u>0.8</u>	-	0.01	525	5

* Minimum Sn concentration in Sn-concentrated layer

(Note) The underlined shows values outside the scope of the invention.

[0074] Test results are shown in Table 1-2. The grain size number shows the measurements on the specimen cut out from the cold-rolled steel sheet. When the specimen subjected to the heat treatment was assessed in terms of the grain size number, the same results as those of the specimen of the cold-rolled steel sheet not subjected to the heat treatment were obtained. It should be noted that, since the Sn-concentrated layer was not formed in Comparative Examples 5 and 6, the Sn concentration at and near the border between the oxide film and the base material is described in Comparative

Examples 5 and 6.

[0075] As shown in Table 1-2, inventive Examples 1 to 18 show 400 μm or less of the maximum pit depth and 6 or more of RN and are thus excellent in corrosion resistance. Comparative Example 1 whose Sn content does not satisfy the requirements of the invention, Comparative Example 2 whose Cr content does not satisfy the requirements of the invention, Comparative Example 3 whose Si content does not satisfy the requirements of the invention, Comparative Example 5 whose heating condition does not satisfy the formula (I) and Comparative Example 6 whose cooling rate in the temperature range from 800 to 600 degrees C during the finish annealing step exceeds 20 degrees C/s all show the maximum pit depth of more than 500 μm and 5 or less of RN and thus are inferior in corrosion resistance. Though the Sn-concentrated layer is formed in Comparative Example 4 whose grain size number is 4, the Sn concentration is not sufficient due to the influence of the grain size number. Consequently, though a certain degree of the pitting corrosion resistance is ensured as shown by the 400 to 500 μm of the maximum pit depth, Comparative Example 4 is inferior in rust resistance as shown by the RN of 5.

INDUSTRIAL APPLICABILITY

[0076] Ferritic stainless steel of the invention is suitable for exhaust system components of an automobile, a motor cycle, a commercial vehicle, a construction machine and the like that are subjected to heating in use. Examples of suitable exhaust system components include a converter case, a front pipe, a center pipe and a muffler.

Claims

1. A ferritic stainless steel for exhaust system components excellent in corrosion resistance after heating, the ferritic stainless steel comprising:

0.015 mass% or less of C;
 0.02 mass% or less of N;
 0.03 mass% to 1.0 mass% of Si;
 1.0 mass% or less of Mn;
 0.04 mass% or less of P;
 0.01 mass% or less of S;
 10.5 mass% to 22.5 mass% of Cr;
 0.02 mass% to 0.5 mass% of Sn;
 0.003 mass% to 0.2 mass% of Al;
 one or both of 0.03 mass% to 0.35 mass% of Ti and 0.03 mass% to 0.6 mass% of Nb; and
 a remnant comprising Fe and inevitable impurities, wherein
 a grain size number on a surface of the ferritic stainless steel is 6 or more, and 2 to 15 nm of a layer containing Sn at a concentration twice or more of a Sn concentration in a base material is formed on the ferritic stainless steel when the ferritic stainless steel is heated in the atmosphere under a condition satisfying a formula (I),

$$\exp(-23000 / T) \times t \geq 4.3 \times 10^{-15} \dots(I)$$

where T represents a temperature (K) and t represents a time (s).

2. A ferritic stainless steel for exhaust system components excellent in corrosion resistance after heating, the ferritic stainless steel comprising:

0.015 mass% or less of C;
 0.02 mass% or less of N;
 0.03 mass% to 1.0 mass% of Si;
 1.0 mass% or less of Mn;
 0.04 mass% or less of P;
 0.01 mass% or less of S;
 10.5 mass% to 22.5 mass% of Cr;
 0.02 mass% to 0.5 mass% of Sn;
 0.003 mass% to 0.2 mass% of Al;

one or both of 0.03 mass% to 0.35 mass% of Ti and 0.03 mass% to 0.6 mass% of Nb; and
a remnant comprising Fe and inevitable impurities, wherein
a grain size number on a surface of the ferritic stainless steel is 6 or more, and
2 to 15 nm of a layer containing Sn at a concentration twice or more of a Sn concentration in a base material
is formed on the ferritic stainless steel.

3. The ferritic stainless steel for exhaust system components excellent in corrosion resistance after heating according to claim 1 or 2, further comprising at least one of a first group and a second group, the first group consisting of one or more of 0.05 mass% to 1.5 mass% of Cu, 0.1 mass% to 1.2 mass% of Ni, 0.03 mass% to 3 mass% of Mo, 0.03 mass% to 1 mass% of W, 0.05 mass% to 0.5 mass% of V and 0.01 mass% to 0.5 mass% of Sb, the second group consisting of one or more of 0.03 mass% to 0.5 mass% of Zr, 0.02 mass% to 0.2 mass% of Co, 0.0002 mass% to 0.002 mass% of Ca, 0.0002 mass% to 0.002 mass% of Mg, 0.0002 mass% to 0.005 mass% of B, 0.001 mass% to 0.01 mass% of REM, 0.0002 mass% to 0.01 mass% of Ga and 0.01 mass% to 0.5 mass% of Ta.

4. The ferritic stainless steel for exhaust system components excellent in corrosion resistance after heating according to any one of claims 1 to 3, wherein the Sn content is 0.02 mass% or more and less than 0.05 mass% and/or 0.07 mass% or more and 0.3 mass% or less.

5. The ferritic stainless steel for exhaust system components excellent in corrosion resistance after heating according to claim 3 or 4, wherein the Ni content is 0.1 mass% or more and less than 0.5 mass%.

6. An exhaust system component excellent in corrosion resistance after heating, the exhaust system component being made from a ferritic stainless steel, the ferritic stainless steel comprising:

0.015 mass% or less of C;
0.02 mass% or less of N;
0.03 mass% to 1.0 mass% of Si;
1.0 mass% or less of Mn;
0.04 mass% or less of P;
0.01 mass% or less of S;
10.5 mass% to 22.5 mass% of Cr;
0.02 mass% to 0.5 mass% of Sn;
0.003 mass% to 0.2 mass% of Al;
one or both of 0.03 mass% to 0.35 mass% of Ti and 0.03 mass% to 0.6 mass% of Nb; and
a remnant comprising Fe and inevitable impurities, wherein
a grain size number on a surface of the ferritic stainless steel is 6 or more, and
2 to 15 nm of a layer containing Sn at a concentration twice or more of a Sn concentration in a base material
is formed on the ferritic stainless steel.

7. The exhaust system component excellent in corrosion resistance after heating and being made from the ferritic stainless steel according to claim 6, wherein the ferritic stainless steel further comprises at least one of a first group and a second group, the first group consisting of one or more of 0.05 mass% to 1.5 mass% of Cu, 0.1 mass% to 1.2 mass% of Ni, 0.03 mass% to 3 mass% of Mo, 0.03 mass% to 1 mass% of W, 0.05 mass% to 0.5 mass% of V and 0.01 mass% to 0.5 mass% of Sb, the second group consisting of one or more of 0.03 mass% to 0.5 mass% of Zr, 0.02 mass% to 0.2 mass% of Co, 0.0002 mass% to 0.002 mass% of Ca, 0.0002 mass% to 0.002 mass% of Mg, 0.0002 mass% to 0.005 mass% of B, 0.001 mass% to 0.01 mass% of REM, 0.0002 mass% to 0.01 mass% of Ga and 0.01 mass% to 0.5 mass% of Ta.

8. The exhaust system component excellent in corrosion resistance after heating and being made from the ferritic stainless steel according to claim 6 or 7, wherein the Sn content is 0.02 mass% or more and less than 0.05 mass% and/or 0.07 mass% or more and 0.3 mass% or less.

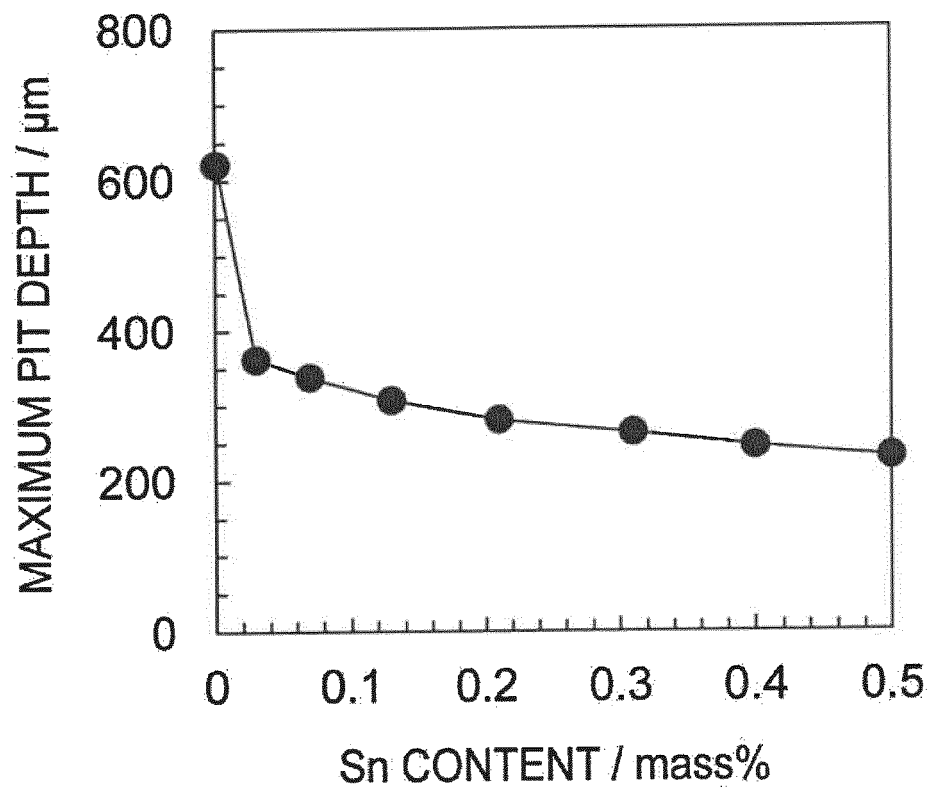
9. The exhaust system component excellent in corrosion resistance after heating and being made from the ferritic stainless steel according to claim 7 or 8, wherein the Ni content is 0.1 mass% or more and less than 0.5 mass%.

10. A manufacturing method of the ferritic stainless steel for exhaust system components excellent in corrosion resistance after heating according to any one of claims 1 to 5, wherein
when the ferritic stainless steel according to any one of claims 1 to 5 is manufactured, a finish annealing temperature

in a cold rolling step is 1030 degrees C or less, and
when the ferritic stainless steel is cooled from a cold-rolled-sheet annealing temperature, a cooling rate in a temperature range from 800 to 600 degrees C is less than 20 degrees C/s.

- 5 11. A manufacturing method of the ferritic stainless steel for exhaust system components excellent in corrosion resistance after heating according to any one of claims 1 to 5, wherein
when the ferritic stainless steel according to any one of claims 1 to 5 is manufactured, a finish annealing temperature in a cold rolling step is 1030 degrees C or less, and
when the ferritic stainless steel is cooled from a cold-rolled-sheet annealing temperature, a cooling rate in a temperature range from 800 to 600 degrees C is less than 5 degrees C/s.
10
12. A manufacturing method of the exhaust system component excellent in corrosion resistance after heating and being made from the ferritic stainless steel according to any one of claims 6 to 9, wherein,
when the ferritic stainless steel forming the exhaust system component according to any one of claims 6 to 9 is
15 manufactured, a finish annealing temperature in a cold rolling step is 1030 degrees C or less, and
when the ferritic stainless steel is cooled from a cold-rolled-sheet annealing temperature, a cooling rate in a temperature range from 800 to 600 degrees C is less than 20 degrees C/s.
- 20 13. A manufacturing method of the exhaust system component excellent in corrosion resistance after heating and being made from the ferritic stainless steel according to any one of claims 6 to 9, wherein
when the ferritic stainless steel forming the exhaust system component according to any one of claims 6 to 9 is manufactured, a finish annealing temperature in a cold rolling step is 1030 degrees C or less, and
when the ferritic stainless steel is cooled from a cold-rolled-sheet annealing temperature, a cooling rate in a temperature range from 800 to 600 degrees C is less than 5 degrees C/s.
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FIG. 1



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2016/051086

A. CLASSIFICATION OF SUBJECT MATTER

C22C38/00(2006.01)i, C21D9/46(2006.01)i, C22C38/28(2006.01)i, C22C38/60(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)
C22C38/00-C22C38/60

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.
X A	WO 2012/036313 A1 (Nippon Steel & Sumikin Stainless Steel Corp.), 22 March 2012 (22.03.2012), 0002, 0042; table 1, invention steel No.13 & US 2013/0149187 A1 paragraphs [0002], [0047]; table 1, Inv.steel No.13 & EP 2617854 A1 & CN 103097564 A & KR 10-2013-0060290 A & JP 5709875 B2	3, 5 1-2, 4, 6-13

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

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	"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
"E" earlier application or patent but published on or after the international filing date	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&" document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search
06 April 2016 (06.04.16)

Date of mailing of the international search report
19 April 2016 (19.04.16)

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Authorized officer

Telephone No.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2016/051086

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X A	JP 2011-202257 A (Nippon Steel & Sumikin Stainless Steel Corp.), 13 October 2011 (13.10.2011), paragraphs [0002], [0032]; table 1, invention steel No.10 & US 2013/0008573 A1 paragraphs [0002], [0101]; table 1, Inv. Steel No.10 & WO 2011/118854 A1 & EP 2557189 A1 & CN 102971441 A & KR 10-2012-0120456 A	3-4 1-2, 5-13
X A	JP 2013-204059 A (Nippon Steel & Sumikin Stainless Steel Corp.), 07 October 2013 (07.10.2013), paragraphs [0002], [0046]; table 1, invention example No.12, 15; comparative example No.41 (Family: none)	3-5 1-2, 6-13
X A	JP 2009-235555 A (Nippon Steel & Sumikin Stainless Steel Corp.), 15 October 2009 (15.10.2009), paragraphs [0002], [0038]; table 1, invention example No.13 (Family: none)	3, 5 1-2, 4, 6-13
X A	JP 2010-031315 A (Nippon Steel & Sumikin Stainless Steel Corp.), 12 February 2010 (12.02.2010), paragraph [0001]; table 1, the present invention No.2 to 4, 6 to 7, 11 to 12, 14, 19, 21 to 24 (Family: none)	1, 3-5 2, 6-13
X A	JP 2014-162964 A (Nippon Steel & Sumikin Stainless Steel Corp.), 08 September 2014 (08.09.2014), paragraph [0001]; table 2, comparative example No.103, 122 to 124, 126 to 128 (Family: none)	1, 4 2-3, 5-13
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Form PCT/ISA/210 (continuation of second sheet) (January 2015)

REFERENCES CITED IN THE DESCRIPTION

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