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(54) **FERRITIC STAINLESS STEEL SHEET AND MANUFACTURING METHOD THEREFOR**

(57) Provided is a ferritic stainless steel sheet which has good surface quality and can prevent coloration due to heating, and a method for producing the same.

The ferritic stainless steel sheet is a ferritic stainless steel sheet which is temper rolled after bright annealing and has a passivation film. The area ratio of minute defects having an area of 10  $\mu\text{m}^2$  or more on the surface of the steel sheet is 0.2% or more and 1.5% or less. In addition, the thickness of the passivation film is 1 nm or more and 10 nm or less, the average concentration of Si

in the passivation film is 10 at% or more and 20 at% or less, and the average concentration ratio of Si, Al, Cr and Fe in the passivation film component is  $(\text{Si} + \text{Al} + \text{Cr}) / \text{Fe} > 1.0$ . When producing this ferritic stainless steel sheet, a hot rolled pickled material is used as a starting material and the surface of the steel sheet is mechanical polished at least once or more in a step preceding finishing cold rolling, followed by annealing. After this annealing, finishing cold rolling, bright annealing and temper rolling are carried out in said order.

**EP 3 480 329 A1**

## Description

### TECHNICAL FIELD

5     **[0001]** The present invention relates to a ferritic stainless steel sheet used for trim, or the like, for example, and a method for producing the same.

### BACKGROUND ART

10    **[0002]** Since a high-Cr ferritic stainless steel sheet used for trim, such as a car molding material, or the like, is required to have a beautiful surface appearance, a highly smooth BA (bright annealing) material is used. Therefore, the requirements towards surface quality, such as minute defects on the surface, the appearance, or the like, are strict, and the surface of a cold rolled sheet is subjected to mechanical polishing during the production process to remove surface scratches.

15    **[0003]** However, since a hard layer is generated in polishing marks by the mechanical polishing, when rolling such as finishing cold rolling and temper rolling is carried out after mechanical polishing, for example, it is thought that there is a possibility that minute surface cracking is generated and the cracking becomes a scratch-shaped minute defect, thereby deteriorating the surface quality of end products.

20    **[0004]** Therefore, as described in PTLs 1 and 2, for example, a method for softening the hard layer in the polishing marks by annealing after mechanical polishing is known.

**[0005]** In addition, in trim such as a molding material, there also are cases where high-frequency heating is carried out at a low temperature to bond a metal part and a non-metal part such as rubber or resin in the production process of its end product, and during this, there also develops a problem that yellow coloration is produced on the surface of the metal part.

25    **[0006]** Such yellow coloration on the surface is thought to be the so-called temper color, and as a method for preventing it, a method in which the composition of a passivation film is controlled by specifying the components and the bright annealing condition, as described in PTLs 3 and 4, for example, is known.

### CITATION LIST

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#### Patent Literature

#### **[0007]**

35     PTL 1: Japanese Examined Patent Publication No. 2-22128  
       PTL 2: Japanese Laid-open Patent Publication No. 9-125150  
       PTL 3: Japanese Laid-open Patent Publication No. 8-295999  
       PTL 4: Japanese Patent No. 3939557

### 40     SUMMARY OF INVENTION

#### Technical Problem

45    **[0008]** By the method in PTLs 1 and 2, however, surface defects due to a hard layer in polishing marks can be reduced, but it is thought that it is difficult to reduce surface defects such as oil pits.

**[0009]** In addition, by the method in PTLs 3 and 4, coloration due to heating can be prevented, but it is thought that it is difficult to reduce other surface defects.

**[0010]** Therefore, a ferritic stainless steel sheet which has good surface quality and can prevent coloration due to heating, and its method have been required.

50    **[0011]** The present invention was made in view of such points, and an object thereof is to provide a ferritic stainless steel sheet which has good surface quality and can prevent coloration due to heating, and a method for producing the same .

#### Solution to Problem

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**[0012]** The ferritic stainless steel sheet described in claim 1 is a ferritic stainless steel sheet which is temper rolled after bright annealing and has a passivation film, wherein the area ratio of minute defects having an area of 10  $\mu\text{m}^2$  or more on the surface of the steel sheet is 0.2% or more and 1.5% or less, the thickness of the passivation film is 1 nm

or more and 10 nm or less, the average concentration of Si in the passivation film is 10 at% or more and 20 at% or less, and the average concentration ratio of Si, Al, Cr and Fe in the passivation film component is  $(\text{Si} + \text{Al} + \text{Cr})/\text{Fe} > 1.0$ .

**[0013]** The ferritic stainless steel sheet described in claim 2 is the ferritic stainless steel sheet described in claim 1, which contains Cr: 17.0 mass% or more and 21.0 mass% or less, Si: 0.2 mass% or more and 1.0 mass% or less, Al: 0.03 mass% or less, C: 0.03 mass% or less, and N: 0.03 mass% or less.

**[0014]** The ferritic stainless steel sheet described in claim 3 is the ferritic stainless steel sheet described in claim 1 or 2, which contains at least one of Nb: 0.1 mass% or more and 1.0 mass% or less, and Cu: 1.0 mass% or less.

**[0015]** The ferritic stainless steel sheet described in claim 4 is the ferritic stainless steel sheet described in any one of claims 1 to 3, which contains Mo: 3.0 mass% or less.

**[0016]** The ferritic stainless steel sheet described in claim 5 is the ferritic stainless steel sheet described in any one of claims 1 to 4, which is for trim and for a car molding material.

**[0017]** The method for producing a ferritic stainless steel sheet described in claim 6 is a method for producing a ferritic stainless steel sheet in which a hot rolled pickled material is used as a starting material and at least finishing cold rolling, bright annealing and temper rolling are carried out in said order, wherein the surface of the steel sheet is mechanical polished at least once in a step preceding finishing cold rolling, followed by annealing.

**[0018]** The method for producing a ferritic stainless steel sheet described in claim 7 is the method for producing a ferritic stainless steel sheet described in claim 6, wherein a total cold rolling reduction until bright annealing is 70% or more, and a cold rolling reduction in finishing cold rolling is 30% or more.

**[0019]** The method for producing a ferritic stainless steel sheet described in claim 8 is the method for producing a ferritic stainless steel sheet described in claim 6 or 7, wherein in the final pass of finishing cold rolling, rolling is carried out using a work roll with an arithmetic average roughness Ra of 0.1  $\mu\text{m}$  or less at a rolling reduction of 12% or more and a rolling speed of 150 m/min or less.

**[0020]** The method for producing a ferritic stainless steel sheet described in claim 9 is the method for producing a ferritic stainless steel sheet described in any one of claims 6 to 8, wherein bright annealing is carried out in a hydrogen and nitrogen mixed gas with a hydrogen concentration of 75% or more at a dew point of  $-45^{\circ}\text{C}$  or lower and an annealing temperature of  $800^{\circ}\text{C}$  or higher and  $990^{\circ}\text{C}$  or lower.

**[0021]** The method for producing a ferritic stainless steel sheet described in claim 10 is the method for producing a ferritic stainless steel sheet described in any one of claims 6 to 9, wherein temper rolling is carried out using a work roll with an arithmetic average roughness Ra of 0.1  $\mu\text{m}$  or less under the condition that the elongation rate be 0.1% or more and 1.0% or less without lubrication.

#### Advantageous Effects of Invention

**[0022]** According to the present invention, since the area ratio of minute defects having an area of 10  $\mu\text{m}^2$  or more on the surface of a steel sheet is 0.2% or more and 1.5% or less, surface quality is good, and since the thickness of a passivation film and the passivation film component are within a predetermined range, coloration due to heating can be prevented.

#### BRIEF DESCRIPTION OF DRAWINGS

##### **[0023]**

Figs. 1(a) and (b) are schematic diagrams which show a surface shape and cross-sectional shape of a hot rolled pickled material.

Figs. 2(a) and (b) are schematic diagrams which show a surface shape and a cross-sectional shape when a hot rolled pickled material is cold-rolled.

Figs. 3(a) and (b) are schematic diagrams which show a surface shape and a cross-sectional shape when intermediate annealing, finishing rolling and bright annealing are carried out following Figs. 2.

Fig. 4 is a schematic diagram which shows a surface shape after mechanical polishing of the surface of a steel sheet having minute defects such as those in Figs. 1, Figs. 2 and Figs. 3.

Fig. 5 is a schematic diagram which shows a surface shape when cold rolling is carried out following Fig. 4.

Fig. 6 is a schematic diagram which shows a surface shape when intermediate annealing, finishing rolling and bright annealing are carried out following Fig. 5.

#### DESCRIPTION OF EMBODIMENTS

**[0024]** The constitution of an embodiment of the present invention will now be described in detail.

**[0025]** A ferritic stainless steel sheet according to this embodiment is used as a material for trim such as a car molding

material, or the like, for example, and is temper-rolled after finishing cold rolling and bright annealing and has a passivation film on a surface layer.

**[0026]** In addition, on the surface of a ferritic stainless steel sheet, the area ratio of minute defects having an area of  $10\ \mu\text{m}^2$  or more is 0.2% or more and 1.5% or less.

**[0027]** Furthermore, the thickness of the passivation film is 1 nm or more and 10 nm or less, the average concentration of Si in the passivation film is 10 at% or more and 20 at% or less, and the average concentration ratio of Si, Al, Cr and Fe in the passivation film component is  $(\text{Si} + \text{Al} + \text{Cr})/\text{Fe} > 1.0$ .

**[0028]** The appearance of a steel sheet is affected by minute defects on the surface of the steel sheet, and particularly, as the number of minute defects having an area of  $10\ \mu\text{m}^2$  or more, which is generally considered as a visually detectable size, increases, the appearance becomes deteriorated.

**[0029]** The area ratio of minute defects is calculated by the sum total area of minute defects having  $10\ \mu\text{m}^2$  or more in a predetermined field of view by an optical microscope.

**[0030]** When the area ratio of minute defects having an area of  $10\ \mu\text{m}^2$  or more is above 1.5%, minute defects which can be visually detected increase and thus the appearance is deteriorated, and there is a possibility that is not suitable as a surface state of an end product. On the other hand, when the area ratio of minute defects having  $10\ \mu\text{m}^2$  or more is about 0.2%, it becomes difficult to visually detect changes in appearances due to minute defects, and therefore, there are no significant changes in appearance of the end product even if the area ratio of minute defects is reduced to lower than 0.2%. In addition, as cold rolling is carried out at a lower speed to reduce minute defects, production costs increase. Therefore, the area ratio of minute defects having an area of  $10\ \mu\text{m}^2$  or more on the surface of a steel sheet is 0.2% or more and 1.5% or less.

**[0031]** It should be noted that, as methods for measuring the area ratio of minute defects, methods in which, for example, photographs of the surface of a steel sheet are taken for 10 or more fields of view by a 50-fold optical microscope, followed by binarization, and the area ratio is measured by the total sum of minute pit portions which became black while having an area of  $10\ \mu\text{m}^2$  or more, or the like, are adopted.

**[0032]** The passivation film prevents coloration produced by, for example, applying an adhesive and heating by high-frequency heating, or the like, when producing an end product.

**[0033]** In order to prevent such coloration, the thickness of the passivation film is required to be 1 nm or more. In addition, as the thickness of the passivation film increases, the prevention of coloration due to heating becomes effective. However, it is required to delay the sheet passing speed in bright annealing to increase its thickness. In order to obtain a passivation film with a thickness of above 10 nm, production costs increase, and there is a possibility that production cannot be efficiently carried out. Therefore, the thickness of the passivation film is 1 nm or more and 10 nm or less.

**[0034]** It should be noted that the thickness of a passivation film is, based on XPS (X-ray Photoelectron Spectroscopy) analysis, the thickness of the portion wherein the concentration of O is reduced to half the maximum concentration of O with regards to the concentration ratio (at%) of O, Fe, Cr, Si, Al, Nb, Mn, N, Cu, or the like, except for the concentration of C, in the passivation film.

**[0035]** In addition, the concentrations of Si, Al, Cr and Fe in a passivation film are important in order to prevent coloration due to warming.

**[0036]** Specifically, Si, Al and Cr are useful to prevent coloration due to warming with a passivation film, and Fe inhibits the action of preventing coloration due to warming with a passivation film.

**[0037]** When the average concentration of Si in a passivation film is 10 at% or more, the action of preventing coloration by the passivation film is good, and when the average concentration of Si in a passivation film is above 20 at%, there is a possibility that production cannot be efficiently carried out because of an increase in production costs. Therefore, the concentration of Si in a passivation film is 10 at% or more and 20 at% or less.

**[0038]** In addition, when the value of  $(\text{Si} + \text{Al} + \text{Cr})/\text{Fe}$  is less than 1.0, since the action of preventing coloration by Si, Al and Cr in a passivation film is weaker than the action of inhibiting the prevention of coloration by Fe in the passivation film, there is a possibility that coloration due to warming cannot be effectively prevented by the passivation film. Therefore, the relationship of the average concentration ratio of Si, Al, Cr and Fe in the passivation film component is  $(\text{Si} + \text{Al} + \text{Cr})/\text{Fe} > 1.0$ .

**[0039]** It should be noted that the average concentrations of Si, Al, Cr and Fe in a film are calculated by the average concentrations, except for the concentration of C, from the surface layer to the thickness of a passivation film.

**[0040]** The components of the above ferritic stainless steel sheet will now be described.

**[0041]** It is preferred that the above ferritic stainless steel sheet have a constitution containing 17.0 mass% or more and 21.0 mass% or less of Cr (chromium), 0.2 mass% or more and 1.0 mass% or less of Si (silicon), 0.03 mass% or less of Al (aluminum), 0.03 mass% or less of C (carbon) and 0.03 mass% or less of N (nitrogen), and comprising Fe (iron) and inevitable impurities as the balance.

**[0042]** In addition, the ferritic stainless steel sheet can also contain 0.1 mass% or more and 1.0 mass% or less of Nb (niobium), and 1.0 mass% or less of Cu (copper) and contain 3.0 mass% or less of Mo (molybdenum) as needed.

**[0043]** Cr is important to obtain good corrosion resistance, and it is required that 17.0 mass% or more of Cr is contained

to display corrosion resistance suitable for trim, a car molding material, or the like. However, when Cr is excessively added to surpass 21.0 mass%, there is a possibility that the steel sheet becomes hard, thereby deteriorating workability. Therefore, the Cr content is 17.0 mass% or more and 21.0 mass% or less.

**[0044]** Si is an element which stabilizes the amount of Si in a passivation film to obtain the action of preventing coloration by the passivation film, and it is required to contain 0.2 mass% or more of Si to display such action. However, when the Si content is above 1.0 mass%, there is a possibility that the steel sheet becomes hard, thereby deteriorating workability. Therefore, the Si content is 0.2 mass% or more and 1.0 mass% or less.

**[0045]** Al has a large effect on non-metal inclusions which cause minute defects (surface scratches) on the surface of a steel sheet, and when the Al content is above 0.03 mass%, there is a possibility that non-metal inclusions are easily formed. Therefore, the Al content is 0.03 mass% or less.

**[0046]** C and N are elements which improve strength; however, when each content is above 0.03 mass%, there is a possibility that workability is reduced. Therefore, the C content and the N content are 0.03 mass% or less each.

**[0047]** Nb has the action of fixing C and N, and is contained as needed to improve corrosion resistance. In addition, it is required to contain 0.1 mass% or more of Nb to display such action; however, when Nb is excessively contained to surpass 1.0 mass%, there is a possibility that workability is reduced. Therefore, the Nb content is 0.1 mass% or more and 1.0 mass% or less.

**[0048]** Cu is contained as needed to improve corrosion resistance, and the content thereof is 1.0 mass% or less.

**[0049]** Mo is contained as needed to improve corrosion resistance, and the content thereof is 3.0 mass% or less.

**[0050]** The method for producing the above ferritic stainless steel sheet will now be described.

**[0051]** When producing the above ferritic stainless steel sheet, in a production method in which a hot rolled pickled material produced by a conventional method is used as a starting material and finishing cold rolling, bright annealing and temper rolling are ultimately carried out in said order, the surface of the steel sheet is mechanical polished at least once or more in a step preceding finishing cold rolling, followed by annealing.

**[0052]** As specific examples of production procedures, the following production procedures are provided, for example.

**[0053]**

(1) [Hot rolled pickled material] -> mechanical polishing -> intermediate annealing -> finishing cold rolling -> bright annealing -> temper rolling,

(2) [hot rolled pickled material] -> intermediate rolling -> mechanical polishing -> intermediate annealing -> finishing cold rolling -> bright annealing -> temper rolling,

(3) [hot rolled pickled material] -> intermediate rolling 1 -> intermediate annealing 1 -> intermediate rolling 2 -> mechanical polishing -> intermediate annealing 2 -> finishing cold rolling -> bright annealing -> temper rolling, and

(4) [hot rolled pickled material] -> mechanical polishing -> intermediate annealing 1 -> intermediate rolling 1 -> intermediate annealing 2 -> finishing cold rolling -> bright annealing -> temper rolling.

**[0054]** That is, for example, as described in the above production procedure (1), when the cold rolling step constitutes solely of finishing cold rolling, mechanical polishing and intermediate annealing are carried out before finishing cold rolling, such as in the order of steps wherein a hot rolled pickled material is subjected to polishing treatment such as mechanical polishing, followed by intermediate annealing, then finishing cold rolling, then bright annealing, and then temper rolling.

**[0055]** In addition, for example, when the cold rolling step is carried out several times such as intermediate cold rolling and finishing cold rolling, there are a process in which mechanical polishing is carried out after intermediate rolling, followed by intermediate annealing, and then finishing cold rolling as described in the above production procedures (2) and (3), a process in which intermediate annealing and intermediate rolling are carried out after mechanical polishing, followed by finishing cold rolling, as described in the above production procedure (4), or the like.

**[0056]** As described in the above production procedures, it is important that, after surface scratches are removed by mechanical polishing, intermediate annealing is carried out before cold rolling.

**[0057]** Here, in a hot rolled pickled material, a shot mark 1 by shot blasting and burrs 2 are generated on the surface of a steel sheet as shown in Figs. 1(a) and (b).

**[0058]** When cold rolling is carried out with such a shot mark 1 and burrs 2 generated, the shot mark 1 and burrs 2 remain in a crushed form as shown in Figs. 2(a) and (b), and these surface defects are drawn out by the cold rolling that follows, generating a scab-shaped defect 3 as shown in Figs. 3(a) and (b).

**[0059]** In addition, when mechanical polishing is carried out on the surface on which the shot mark 1, burrs 2 and scab-shaped defect 3 are generated as shown in Figs. 1 to 3, although these shot mark 1, burrs 2 and scab-shaped defect 3 are removed as shown in Fig. 4, a hard layer is generated in the polishing marks.

**[0060]** When cold rolling is carried out in a state where a hard layer is generated as described above, minute cracking 4 occurs on the surface of the steel sheet as shown in Fig. 5, and the cracking opens as the cold rolling progresses.

**[0061]** Then, when cold rolling is further carried out in a state where minute cracking 4 has occurred, the minute

cracking 4 is drawn out to become a scratch-shaped defect 5 as shown in Fig. 6.

**[0062]** Therefore, by annealing after removing the shot mark 1, burrs 2 and scab-shaped defect 3 remaining in the hot rolled pickled material and its cold rolled material by mechanical polishing, the hard layer in polishing marks is recrystallized, and the occurrence of minute cracking 4 and the scratch-shaped defect 5 in the cold rolling that follows can be prevented, thereby obtaining beautiful surface quality.

**[0063]** It should be noted that the frequency of mechanical polishing can be appropriately decided depending on the states of the shot mark 1, burrs 2 and scab-shaped defect 3 remaining in a hot rolled pickled material and its cold rolled material as well as desired performance and states.

**[0064]** In addition, the annealing after mechanical polishing can be carried out either by a method of annealing and pickling in an atmosphere which is not adjusted, or a method of bright annealing in a hydrogen atmosphere; however, it is important not to newly generate minute surface defects by, for example, excessive heating, pickling, descaling, or the like.

**[0065]** Furthermore, in order to obtain beautiful surface quality of a ferritic stainless steel sheet, it is preferred that cold rolling be carried out under a predetermined condition so that oil pits and other minute defects can be reduced by drawing out minute defects on the surface of the steel sheet.

**[0066]** Specifically, it is preferred that the total cold rolling reduction from the hot rolled pickled material until bright annealing be 70% or more, and the cold rolling reduction in finishing cold rolling be 30% or more.

**[0067]** Furthermore, it is preferred that, in the final pass of finishing cold rolling, rolling be carried out using a work roll with an arithmetic average roughness Ra of 0.1  $\mu\text{m}$  or less at rolling reduction of 12% or more and a rolling speed of 150 m/min or less.

**[0068]** In addition, it is preferred that bright annealing be carried out under a predetermined condition to form a passivation film which effectively prevents coloration due to heating.

**[0069]** Specifically, it is preferred that bright annealing be carried out in a hydrogen and nitrogen mixed gas with a hydrogen concentration of 75% or more at a dew point of  $-45^{\circ}\text{C}$  or lower and an annealing temperature of  $800^{\circ}\text{C}$  or higher and  $990^{\circ}\text{C}$  or lower. It should be noted that the temperature of bright annealing described in the present invention points to the highest temperature to which a stainless steel sheet reaches and is controlled by, for example, the temperature of the bright annealing furnace, the sheet passing speed of a stainless steel sheet, or the like.

**[0070]** In addition, it is preferred that temper rolling be carried out under a condition that a passivation film is not broken, since, when a passivation film is broken by temper rolling after bright annealing, coloration due to heating cannot be effectively prevented by the passivation film.

**[0071]** Specifically, it is preferred that temper rolling be carried out using a work roll with an arithmetic average roughness Ra of 0.1  $\mu\text{m}$  or less under the condition that the elongation rate be 0.1% or more and 1.0% or less without lubrication.

**[0072]** Since the area ratio of minute defects having an area of 10  $\mu\text{m}^2$  or more on the surface of a steel sheet is 0.2% or more and 1.5% or less according to an embodiment described above, minute defects such as minute marks, minute cracking and minute pits are limited, and the surface appearance is beautiful as a material for trim such as a car molding material, or the like, and the surface quality is good.

**[0073]** In addition, the thickness of a passivation film is 1 nm or more and 10 nm or less, the average concentration of Si in the passivation film is 10 at% or more and 20 at% or less, and the average concentration ratio of Si, Al, Cr and Fe in the passivation film component is  $(\text{Si} + \text{Al} + \text{Cr})/\text{Fe} > 1.0$ , and thus, the passivation film can prevent the development of coloration due to heating during, for example, heating treatment after applying an adhesive when installing a ferritic stainless steel sheet as a product, or the like.

**[0074]** Furthermore, since the above ferritic stainless steel sheet has good surface quality and can prevent coloration due to heating as described above, it is suitable for trim such as a car molding material, or the like.

**[0075]** When producing a ferritic stainless steel sheet, since, with regards to a hot rolled pickled material, the surface of the steel sheet is mechanical polished in a step preceding finishing cold rolling and is followed by annealing, a hard layer in the polishing marks becomes soft by annealing, and the generation of minute defects by the cold rolling that follows can be prevented. Therefore, beautiful surface quality wherein the area ratio of minute defects having an area of 10  $\mu\text{m}^2$  or more on the surface of the steel sheet is 0.2% or more and 1.5% or less can be obtained.

**[0076]** In cold rolling, by setting the total cold rolling reduction until bright annealing as 70% or more and the cold rolling reduction in finishing cold rolling as 30% or more, minute defects on the surface of a steel sheet can be reduced.

**[0077]** In addition, in the final pass of finishing cold rolling, by carrying out rolling using a work roll with an arithmetic average roughness Ra of 0.1  $\mu\text{m}$  or less at rolling reduction of 12% or more and a rolling speed of 150 m/min or less, minute defects on the surface of a steel sheet can be reduced.

**[0078]** As for bright annealing, by using a hydrogen and nitrogen mixed gas with a hydrogen concentration of 75% or more at a dew point of  $-45^{\circ}\text{C}$  or lower and an annealing temperature of  $800^{\circ}\text{C}$  or higher and  $990^{\circ}\text{C}$  or lower, the amount of Si in a passivation film (the average concentration of Si) is easily adjusted to a range of 10 at% or more and 20 at% or less, the average concentration ratio of Si, Al, Cr and Fe in the passivation film component is easily adjusted to a range of  $(\text{Si} + \text{Al} + \text{Cr})/\text{Fe} > 1.0$ , and the thickness of the passivation film is easily adjusted to a range of 1 nm or more

and 10 nm or less, and thus, a passivation film which can effectively prevent coloration due to heating can be formed.

**[0079]** As for temper rolling, by carrying out rolling using a work roll with an arithmetic average roughness Ra of 0.1  $\mu\text{m}$  or less under the condition that the elongation rate be 0.1% or more and 1.0% or less without lubrication, the passivation film formed by bright annealing is not easily broken, and thus, a passivation film which can effectively prevent coloration due to heating can be retained.

#### Examples

**[0080]** Examples and Comparative Examples thereof will now be described.

**[0081]** A 19 Cr-0.5 Si-0.5 Nb-0.5 Cu stainless steel was smelted in an actual device to obtain a hot rolled pickled material. This hot rolled pickled material was subjected to mechanical polishing in accordance with the above-described production procedures (2) and (4), and stainless steel sheets were produced while changing cold rolling conditions, bright annealing (BA) conditions and temper rolling (SKP, skin pass) conditions.

**[0082]** For each of these stainless steel sheets, the passivation film was investigated and surface quality was evaluated, and thereafter, heating treatment was carried out, and the degree of coloration on the surface was investigated.

**[0083]** As for the evaluation of surface quality, the surface of an end product was observed with an optical microscope, and the area ratio of minute defects having an area of 10  $\mu\text{m}^2$  or more was calculated, and an area ratio of 1.5% or less was evaluated as good surface quality.

**[0084]** As for the evaluation of passivation films, measurement was made by XPS analysis, and evaluation was made based on the thickness of the passivation film, the amount of Si in the passivation film, and the proportion of Si, Al and Cr to Fe in the passivation film (the value of (Si + Al + Cr) / Fe) .

**[0085]** As for the evaluation of the degree of coloration, heating treatment (annealing and pickling) was carried out at 300°C\*0 sec in a laboratory, and a brightness difference ( $\Delta L^*$ ), a red chromaticity difference ( $\Delta a^*$ ) and a yellow chromaticity difference ( $\Delta b^*$ ) before and after the heating treatment were measured to evaluate changes in color on the surface of a steel sheet.

**[0086]** It should be noted that a color difference was measured using a spectrophotometer: CM-2500 d manufactured by KONICA MINOLTA by a method in accordance with JIS Z 8722. Changes in color were evaluated by a color difference ( $\Delta E^*ab$ ) of the formula shown below, and those with a value of 2 or less was determined as good.

$$\Delta E^*ab = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$$

Test conditions and test results for Examples and Comparative Examples are shown in Table 1.

[Table 1]

Sample No.		Procedure	Step after mechanical polishing			Finishing rolling condition			Bright annealing condition	Investigation of results of passivation film			Color difference before and after heating treatment	Category	
			Finishing rolling reduction (%)	Rolling reduction in final pass (%)	Rolling speed in final pass (m/min)	Annealing temperature (°C)	Dew point (°C)	H2 concentration (%)		Film thickness (nm)	Si amount (at%)	(Si + Al + Cr)/Fe			
1	(2)	AP	75	15	100	980	-48	75	0.6	0.8	2.1	11.8	1.7	1.5	Example
2	(4)	BA	80	20	120	950	-55	99	0.9	0.9	3.2	15.2	1.7	0.9	Example
3	(2)	AP	75	25	100	950	-50	75	<u>1.5</u>	0.8	1.3	<u>9.1</u>	<u>0.9</u>	<u>2.8</u>	Comparative Example
4	(2)	BA	75	15	120	950	-40	75	0.5	0.9	3.8	<u>3.5</u>	0.8	<u>3.8</u>	Comparative Example

## EP 3 480 329 A1

5	(2)	AP	75	15	150	<u>1040</u>	-50	75	0.6	1.0	3.8	<u>4.0</u>	<u>0.6</u>	<u>6.3</u>	Comparative Example
6	(4)	AP	50	12	100	930	-55	<u>50</u>	0.7	1.2	<u>11.0</u>	<u>2.0</u>	<u>0.4</u>	<u>6.8</u>	Comparative Example
7	(4)	BA	75	<u>10</u>	<u>250</u>	820	-65	90	0.6	<u>1.9</u>	5.0	14.0	1.1	1.9	Comparative Example
8	(4)	<u>cold</u> <u>rollin</u> <u>g</u>	75	15	120	950	-59	99	0.6	<u>2.2</u>	6.0	13.0	1.2	1.7	Comparative Example

**[0087]** In Sample Nos. 1 and 2, which are Examples in which annealing was carried out after mechanical polishing, and cold rolling, bright annealing and temper rolling were carried out under the conditions within the above predetermined ranges, the area ratio of minute defects was lower than 1.5%, and surface quality was good. In addition, the thickness of a passivation film was within the above range, and as for the passivation film component, the amount of Si was within the above range while the value of (Si + Al + Cr) /Fe was also within the above range, and the value of color difference ( $\Delta E^*ab$ ) before and after heating treatment was lower than 2, changes in color on the surface of a steel sheet being limited.

**[0088]** In Sample No. 3, which is a Comparative Example, since the elongation rate of temper rolling was higher than 1.0%, changes in color on the surface of the steel sheet after heating treatment was significantly greater in comparison to the Examples.

**[0089]** In Sample No. 4, which is a Comparative Example, since the dew point during bright annealing was higher than -45°C, the amount of Si in the passivation film was lower than 10 at%, and in addition, the value of (Si + Al + Cr)/Fe was 1.0 or less, and changes in color on the surface of the steel sheet after heating treatment was significantly greater in comparison to the Examples.

**[0090]** In Sample No. 5, which is a Comparative Example, since the annealing temperature during bright annealing was higher than 990°C, the amount of Si in the passivation film was lower than 10 at%, and changes in color on the surface of the steel sheet after heating treatment was significantly greater in comparison to the Examples.

**[0091]** In Sample No. 6, which is a Comparative Example, since the hydrogen concentration in the mixed gas in bright annealing was lower than 75%, the thickness of the passivation film was thicker than 10 nm, and in addition, the amount of Si in the passivation film was lower than 10 at%, and changes in color on the surface of the steel sheet after heating treatment was significantly greater in comparison to the Examples.

**[0092]** In Sample No. 7, which is a Comparative Example, since the rolling speed of finishing cold rolling was faster than 150 m/min and the rolling reduction of finishing cold rolling was less than 12%, the area ratio of minute defects was higher than 1.5% and surface quality was bad.

**[0093]** In Sample No. 8, which is a Comparative Example, since cold rolling was carried out without annealing after mechanical polishing, the area ratio of minute defects was higher than 1.5%, and surface quality was bad.

### Industrial Applicability

**[0094]** The present invention can be used in a steel sheet required to have a beautiful surface appearance such as those for trim such as a car molding material, or the like.

### Claims

1. A ferritic stainless steel sheet which is temper rolled after bright annealing and has a passivation film, wherein the area ratio of minute defects having an area of 10  $\mu m^2$  or more on the surface of the steel sheet is 0.2% or more and 1.5% or less, the thickness of the passivation film is 1 nm or more and 10 nm or less, the average concentration of Si in the passivation film is 10 at% or more and 20 at% or less, and the average concentration ratio of Si, Al, Cr and Fe in the passivation film component is (Si + Al + Cr)/Fe > 1.0.

2. The ferritic stainless steel sheet according to claim 1, which contains Cr: 17.0 mass% or more and 21.0 mass% or less, Si: 0.2 mass% or more and 1.0 mass% or less, Al: 0.03 mass% or less, C: 0.03 mass% or less, and N: 0.03 mass% or less.

3. The ferritic stainless steel sheet according to claim 1 or 2, which contains at least one of Nb: 0.1 mass% or more and 1.0 mass% or less, and Cu: 1.0 mass% or less.

4. The ferritic stainless steel sheet according to any one of claims 1 to 3, which contains



Mo: 3.0 mass% or less.

- 5      5. The ferritic stainless steel sheet according to any one of claims 1 to 4, which is for trim and for a car molding material.

- 10      6. A method for producing a ferritic stainless steel sheet, in which a hot rolled pickled material is used as a starting material and at least finishing cold rolling, bright annealing and temper rolling are carried out in said order, wherein the surface of the steel sheet is mechanical polished at least once in a step preceding the finishing cold rolling, followed by annealing.

- 15      7. The method for producing a ferritic stainless steel sheet according to claim 6, wherein a total cold rolling reduction until the bright annealing is 70% or more, and a cold rolling reduction in the finishing cold rolling is 30% or more.

- 20      8. The method for producing a ferritic stainless steel sheet according to claim 6 or 7, wherein in a final pass of the finishing cold rolling, rolling is carried out using a work roll with an arithmetic average roughness Ra of 0.1  $\mu\text{m}$  or less at a rolling reduction of 12% or more and a rolling speed of 150 m/min or less.

- 25      9. The method for producing a ferritic stainless steel sheet according to any one of claims 6 to 8, wherein the bright annealing is carried out in a hydrogen and nitrogen mixed gas with a hydrogen concentration of 75% or more at a dew point of  $-45^{\circ}\text{C}$  or lower and an annealing temperature of  $800^{\circ}\text{C}$  or higher and  $990^{\circ}\text{C}$  or lower.

- 30      10. The method for producing a ferritic stainless steel sheet according to any one of claims 6 to 9, wherein the temper rolling is carried out using a work roll with an arithmetic average roughness Ra of 0.1  $\mu\text{m}$  or less under the condition that an elongation rate be 0.1% or more and 1.0% or less without lubrication.

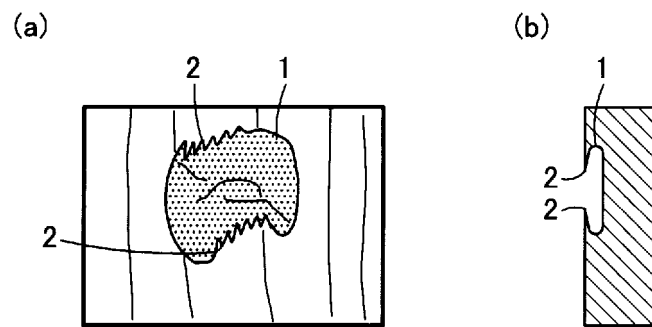


FIG. 1

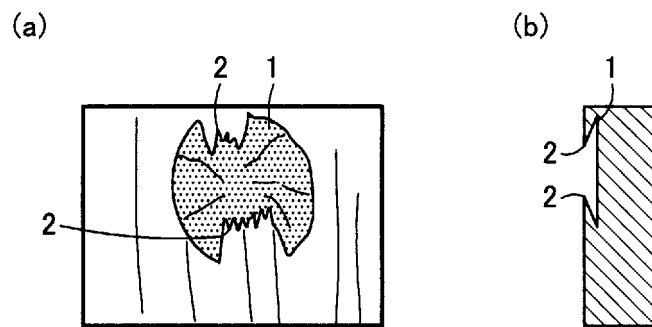


FIG. 2

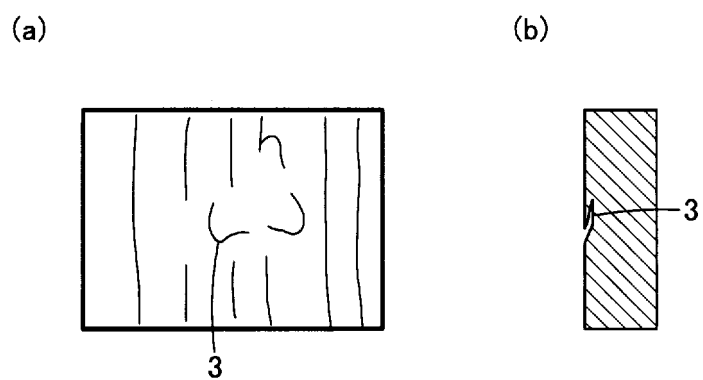


FIG. 3

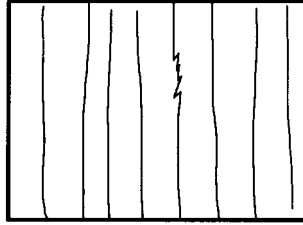


FIG. 4

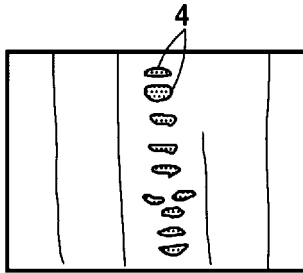


FIG. 5

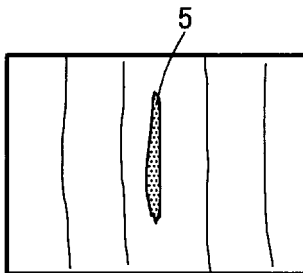


FIG. 6

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2016/087051

## A. CLASSIFICATION OF SUBJECT MATTER

C22C38/00(2006.01)i, C21D9/46(2006.01)i, C22C38/18(2006.01)i, C22C38/26(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, C21D8/02, C21D9/46

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	1996-2017
Kokai Jitsuyo Shinan Koho	1971-2017	Toroku Jitsuyo Shinan Koho	1994-2017

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	JP 2011-214079 A (Nisshin Steel Co., Ltd.),	6-7
Y	27 October 2011 (27.10.2011),	6-10
A	claims; 0001, 0072 to 0089 (Family: none)	1-5
Y	JP 2013-208638 A (Nisshin Steel Co., Ltd.),	6-10
A	10 October 2013 (10.10.2013),	1-5
	claims; 0001, 0016 to 0019, 0039; tables 1 to 2 (Family: none)	

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

\* Special categories of cited documents:

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Date of the actual completion of the international search  
06 March 2017 (06.03.17)Date of mailing of the international search report  
14 March 2017 (14.03.17)Name and mailing address of the ISA/  
Japan Patent Office  
3-4-3, Kasumigaseki, Chiyoda-ku,  
Tokyo 100-8915, Japan

Authorized officer

Telephone No.

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2016/087051

C (Continuation).	DOCUMENTS CONSIDERED TO BE RELEVANT	
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Y A	JP 2005-240062 A (Nisshin Steel Co., Ltd.), 08 September 2005 (08.09.2005), claims; 0019, 0022; table 2 (Family: none)	9-10 1-8
A	JP 2013-208639 A (Nisshin Steel Co., Ltd.), 10 October 2013 (10.10.2013), (Family: none)	1-10
A	JP 11-50202 A (Sumitomo Metal Industries, Ltd.), 23 February 1999 (23.02.1999), (Family: none)	1-10
A	JP 10-259418 A (Nippon Steel Corp.), 29 September 1998 (29.09.1998), & WO 1998/042889 A1 & KR 10-2000-0011127 A & CN 1220706 A	1-10
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Form PCT/ISA/210 (continuation of second sheet) (January 2015)

**REFERENCES CITED IN THE DESCRIPTION**

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- JP 9125150 A [0007]
- JP 8295999 A [0007]
- JP 3939557 B [0007]