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D-81675 München (DE)(54) **STEEL SHEET OF HIGH STRESS-CORROSION-CRACKING RESISTANCE FOR CANS AND METHOD OF MANUFACTURING THE SAME.**(57) A steel sheet of a high stress-corrosion-cracking resistance for cans, characterized in that the steel sheet contains not more than 0.0015 wt.% of C, 0.05-0.40 wt.% of Mn, not more than 0.06 wt.% of P, not more than 0.06 wt.% of S, not more than 0.10 wt.% of acid soluble Al and not more than 0.0100 wt.% of N, at least one of not less than $3.4 \times ((\text{weight percentage of N}) - 0.0010)$ wt.% and not more than 0.06 wt.% of Ti and not less than $6.6 \times ((\text{weight percentage of N}) - 0.0010)$ wt.% and not more than 0.06 wt.% of Nb being further contained as necessary, the rest consisting of iron and unavoidable impurities, the steel sheet having an aging index of not**EP 0 662 523 A1**

less than 15 MPa, the relative average visibility of an electron channeling pattern measured with respect to not less than 20 crystal grains, which are not less than 50 μm away from one another, in an intermediate portion of the steel sheet in the direction of the thickness thereof being not more than 0.85; and a method of manufacturing the steel sheet. The present invention provides a steel sheet for two-piece cans and three-piece cans which has a small thickness and a high stress-corrosion-cracking resistance.

Technical Field

The present invention relates to a thin steel sheet for a two-piece can and a thin steel sheet for a three-piece can, having high resistance to stress corrosion cracking, and a process for producing the same.

Background Art

Steel sheets for cans, such as a tinplate, which is a tinned steel sheet, or a tin-free steel sheet, which is a chromate-treated steel sheet, are used widely in food cans, aerosol cans, easy-open cans, and the like. These cans can be classified roughly into a two-piece can and a three-piece can.

The two-piece can comprises two components of a barrel integral with a bottom and of a cover. By virtue of low can-making cost, there is an ever-increasing tendency for an increase in the proportion of the two-piece can to the whole cans. In the manufacture of the two-piece can, forming under severe conditions, such as multistage drawing or DWI (the abbreviation for drawing and wall ironing; that is, deep drawing followed by ironing), is carried out, requiring for the steel sheet used to have corrosion resistance as well as excellent formability.

An example of a conventional process for producing a DWI can, a representative two-piece can, will now be described.

A blank sheet in a disk form is punched from a steel strip by means of a cupping press. At the same time, the blank sheet is subjected to shallow drawing using a punch and a die to form a cup. Then, the cup is stretched by means of a DWI press while ironing the side wall of the cup using a punch and a die having a smaller clearance than the thickness of the side wall of the cup to reduce the thickness of the side wall, thereby forming a can body having a cup form having a desired depth. This forming is called "DWI." Further, the bottom of the can body is formed by a bottom former into a dome with the bottom being protruded inward.

In DWI, ears are formed by a phenomenon called "earring" wherein the top end of the barrel after forming is waved in a circumferential direction due to the anisotropy of forming of the material. The ear is trimmed with a trimmer to regulate the top end of the barrel.

The can body is then cleaned and dried, and printing and painting are carried out on the external surface of the can. Subsequently, the can is subjected to multistage necking wherein the opening diameter of the can body is reduced with a necker-flanger. Further, in order to provide a cover at the opening end of the can body, flanging is carried out wherein a flange radially extending toward the outside of the can is formed at the opening end.

Important properties required of steel sheets for a DWI can include DWI property, earring property, neck forming property, flange forming property, and, in the form of a can, additionally compressive strength and paneling strength.

These properties will now be described.

The DWI property is a property which, in DWI, is less likely to cause abrasion of a mold and less likely to cause scoring of a mold and requires no large energy in the forming.

The earring property is a property which, in DWI, minimizes earring. Since the ear portion is cut out with a trimmer prior to necking, large earring lowers the yield of the material.

The neck forming property is a property which causes no wrinkle in multistage necking.

The flange forming property is a property which, in flanging, is less likely to cause cracking causative of leakage of the contents of the can into the flange portion, that is, a defect called "flange cracking."

The compressive strength is a critical internal pressure of the can at which, after seaming of the cover, a buckling phenomenon occurs causing weak portions of the can body to be unfavorably protruded outward by internal pressure. The can in its portions weak against the internal pressure are the bottom and cover of the can, and the compressive strength too is, in many cases, governed by the mechanical strength of the bottom and cover of the can.

The paneling strength is a critical external pressure at which, after seaming of the cover, the barrel of the can body is recessed inward by external pressure. In many cases, the strength against external force applied during handling of canned goods, such as packing, transport, unpacking, falling in a vending machine, and the like is represented by the paneling strength.

The three-piece can will now be described.

Since the three-piece can has advantages over the two-piece can, such as higher paneling strength, there is an ever-increasing tendency for an increase in the absolute quantity of the three-piece cans produced.

The production of the three-piece can will be briefly described.

At the outset, predetermined printing and coating of the internal surface are carried out on a steel sheet, and the printed and coated steel sheet is dried. It is then cut with a cutter into a square blank sheet having a desired size in two steps of cutting in the rolling direction and cutting normal to the rolling direction. The square blank sheet is formed by means of a barrel making machine into a cylinder which is then subjected to joining by welding, bonding, soldering, or other methods to prepare a can barrel. Then, the diameter of the opening of the can body is reduced by multistage necking with a necker-flanger. Further, in order to provide a cover at the opening end of the can body, a flange radially extending toward the outside of the can body is formed at the opening end by flanging. Thereafter, one of a cover and a bottom is mounted on the flange portion by means of a double seamer.

The three-piece can can be classified into a welded can, a bonded can, and a soldered can according to the joining method. The width of lapped portion in the joint leads to a lowering in yield of the material, resulting in a gradually increasing tendency for use of the welded can having the smallest width.

Important properties required of the steel sheet for a welded can include weldability, neck forming property, flange forming property, and paneling strength.

The weldability is a property that welding can be carried out in a broad current range, that is, the current range capable of providing satisfactory joint strength and causing no splash is broad. The broader the current range usable in the welding, the more stable the welding operation.

The neck forming property, flange forming property, and paneling strength are as described above.

In both the two-piece can and the three-piece can, from the viewpoint of saving resources, there is an ever-increasing tendency for can manufacturers to demand a thinner steel sheet for a can to can steel sheet manufacturers. A reduction in the sheet thickness, however, unfavorably results in deteriorated earring property, neck forming property, and flange forming property and lowered can strength. For this reason, the supply of steel sheets, for cans, which have a small thickness and can ensure desired earring property, neck forming property, flange forming property, and can strength, has become a large task to be performed.

In order to meet the above demands, the present inventors have proposed an invention in Japanese Patent Application No. 132712/1992 (Japanese Patent Laid-Open No. 345924/1993). This invention relates to a technique where a steel sheet, for a two-piece can, having a small thickness and excellent earring property and DWI property and a very thin steel sheet, for a welded can, having an excellent flange forming property can be provided by combining proper regulation of chemical ingredients, particularly a reduction in C content to the extremity, and addition of Ti, Nb, or B with regulation of conditions for secondary cold rolling.

Subsequent further detailed studies conducted by the present inventors have revealed that a reduction in thickness of the steel sheet for a can often gives rise to stress corrosion cracking, and the conventional techniques including those proposed by the present inventions cannot completely prevent stress corrosion cracking.

Stress corrosion cracking is a failure passing through the sheet in the thicknesswise direction, which failure is a serious defect leading to leakage of the contents of the can and inclusion of foreign materials from the outside of the can. Although the cause of the stress corrosion cracking has not been fully elucidated yet, the stress corrosion cracking is generally said to occur by a combination of several unfavorable conditions in respect of stress in the steel sheet, shape of the can, can forming conditions, composition of the contents, hydrogen ion concentration (pH), and the like. The reason why a reduction in thickness of the steel sheet leads to a problem of stress corrosion cracking is believed to reside in not only the fact that the reduced thickness of the steel sheet facilitates the propagation of the crack through the sheet in the thicknesswise direction but also the special process for producing a steel sheet meeting a demand for a reduction in sheet thickness.

An object of the present invention is to solve the above problems of the prior art and to provide a steel sheet for a two-piece can and a steel sheet for a three-piece can, having a small thickness and high resistance to stress corrosion cracking, and a process for producing the same.

Disclosure of Invention

The steel sheet, for a can, having high resistance to stress corrosion cracking according to the present invention is characterized by comprising, by weight percent, C: not more than 0.0015%, Mn: 0.05 to 0.40%, P: not more than 0.06%, S: not more than 0.06%, sol. Al: not more than 0.10%, and N: not more than 0.0100% and

optionally at least one member selected from Ti: not less than $3.4 \times ([\text{wt}\% \text{ of N}] - 0.0010)\%$ to not more than 0.06% and Nb: not less than $6.6 \times ([\text{wt}\% \text{ of N}] - 0.0010)\%$ to not more than 0.06% with the balance

consisting of iron and unavoidable impurities,

said steel sheet having an aging index of not less than 15 MPa and a relative average sharpness of electron channelling patterns of not more than 0.85 as measured on 20 or more grains located in a central portion of the sheet thickness and not less than 50 μm apart from one another.

5 Other characteristic features of the present invention reside in a process for producing a steel sheet for a can, comprising the steps of: hot-rolling a hot steel slab comprising the above chemical ingredients at a finishing temperature of not less than 810°C to a thickness of not less than 2.0 mm, coiling the resultant hot-rolled steel strip while cooling with water on a run-out table within 1.5 sec or less after emergence from a finishing final stand of a hot rolling machine from a temperature of not less than [finishing temperature -
10 30]°C and subjecting the coiled steel strip to pickling, cold rolling, and recrystallization annealing; and subjecting the annealed steel strip to secondary cold rolling with a reduction ratio of 0.7 to 60% so that the average strain rate (SR) defined by the following equation is not less than 12.4 sec^{-1} :

$$15 \quad SR = \frac{1}{60 \sqrt{r}} \cdot \frac{1000}{\sqrt{R} \cdot \sqrt{t}} \frac{v}{\sqrt{t}} \ln \frac{1}{1-r}$$

wherein

20 r: reduction ratio, -;
R: radius of work roll, mm;
t: sheet thickness on inlet side, mm; and
v: peripheral speed of work roll, m/min.

25 Best Mode for Carrying Out the Invention

The present inventors have found that a close correlation exists between the sharpness of an electron channeling pattern of a steel sheet and the occurrence of stress corrosion cracking. Further, they have systematically investigated the correlation and conducted various experiments on the process for producing
30 a steel sheet. As a result, the following facts were found.

- (1) A steel sheet having a small relative average sharpness of electron channeling patterns has high resistance to stress corrosion cracking.
- (2) The presence of C in a solid solution form and N in a solid solution form in respective amounts exceeding given values is also necessary for the prevention of stress corrosion cracking.
- 35 (3) The regulation of conditions for secondary cold rolling, particularly the average strain rate of the steel in a roll bite, is important for decreasing the sharpness of the electron channeling pattern.
- (4) Proper regulation of chemical ingredients, particularly a reduction in C content to the extremity, and, at the same time, proper regulation of conditions for hot rolling are also necessary to the production of a steel sheet.

40 The present invention has been made base on these novel findings.

The present invention will now be described in more detail.

At the outset, the electron channeling pattern of a steel sheet and the sharpness thereof will be described.

The relative average sharpness of electron channeling patterns (hereinafter referred to as "ECP") is the
45 most important constituent feature of the present invention. Angular scanning of an electron beam onto a crystalline material using a scanning electron microscope causes a channeling phenomenon when the incident angle of the electron beam satisfies Bragg's reflection conditions, forming an image of many pseudo-Kikuchi lines. This image is called an "electron channeling pattern" and utilized in studies on crystal orientation of individual grains.

50 In the case of steel sheets produced on a commercial scale, sharp ECP is not always provided. The space between three sets of parallel pseudo-Kikuchi lines in ECP and the coordinate of the center of a parallelogram formed by intersection of these parallel lines are important to the study of crystal orientation. The unsharpness of ECP is processed as a noise.

The present inventors have found that there is a correlation between the sharpness of ECP and the rate
55 of occurrence of stress corrosion cracking and that a steel sheet, for a can, having a sharpness smaller than a given value has high resistance to stress corrosion cracking.

The sharpness can be quantified by several methods. The present inventors quantified the sharpness by using, among these methods, a method described in an article entitled "ECP Gazo Kaiseki Ni Yoru

Kessho Hizumi Sokutei Hoho (Crystal Strain Measuring Method Using ECP Image Analysis" (Journal of the Japan Institute of Metal, Vol. 55, No. 1 (1991) pp. 22-28).

Specifically, a series of image processing steps of input of an image, density varying image processing, digitization, and digital image processing are carried out using an image analyzer connected on-line with a scanning electron microscope, and the following calculation is carried out:

$$S = L \times W/A$$

wherein L represents the sum of the lengths of sharp pseudo-Kikuchi lines within the ECP image plane, W represents the width of sharp pseudo-Kikuchi lines within the ECP image plane, and A represents the area of the ECP image plane. The quantity S expressed by the equation is defined as sharpness.

In this case, the input of an image refers to average adding input of an ECP image from a scanning electron microscope into an image analyzer.

The density varying image processing refers to a processing involving a series of steps of (1) smoothing the input image with an intermediate-value filter, (2) conducting linear transformation so that the maximum value and the minimum value of the density level are the maximum value and the minimum value of the density level in an image analyzer, (3) conducting selective local averaging, (4) conducting two-dimensional differentiation with a Sobel filter, (5) conducting gamma transformation, log transformation, and again gamma transformation, and (6) finally smoothing again the object image plane with an intermediate-value filter.

The digitization refers to setting of a fixed threshold value with respect of the image after the density varying image processing followed by conversion to two values based on whether the value is larger or smaller than the set value.

The digital image processing refers to a processing involving a series of steps of (1) removing isolated points from the image after the digitization and conducting expansion and contraction processing, (2) conducting smoothing and then padding, and (3) conducting line width reduction processing by the Tamura's method (Shinzendaishi, Vol. 1539 (1974) p. 1390) and finally conducting again expansion processing.

The present inventors used Model TOSPIX-II for the image analysis. The above image processing can be carried out using any image analyzer so far as the image analyzer has an image analyzing capability equal or superior to TOSP IX-II. The sharpness S is a physical quantity for a steel sheet and does not depend upon the type of the image analyzer. Further, the scanning electron microscope need not be necessarily connected on-line with the image analyzer, and the data may be transferred through a medium such as a magnetic tape.

Sharp pseudo-Kikuchi lines are, in fact, nothing but all curves in the image after the above image processing. This is because unsharp pseudo-Kikuchi lines are removed in the course of the image processing. Whether or not the pseudo-Kikuchi line is sharp can be judged based on the threshold value in the digitization. The present inventors used 50 as the threshold value.

The sum L of the lengths of sharp pseudo-Kikuchi lines within an ECP image plane is the sum of the lengths of all intermittent curves in the image after the above image processing. This quantity can be easily determined by means of a conventional image analyzer.

The width W of sharp pseudo-Kikuchi lines within an ECP image plane is a constant and can be easily determined again by a conventional image analyzer.

The area A of an ECP image plane is a constant independent of samples.

X-ray analysis provides information on average crystal orientation of a steel sheet, which is a polycrystalline material. On the other hand, ECP uses a fine electron beam and, hence, has a feature that information on the crystal orientation of individual grains can be provided. As a result, the sharpness S greatly depends upon the orientation of grain irradiated with an electron beam. The orientation of grain, however, has no direct correlation with the stress corrosion cracking. Therefore, in order to correlate the sharpness with the stress corrosion cracking, it is necessary to separate the contribution of the orientation from the sharpness.

For this reason, the present inventors measured the sharpness for 20 or more grains located in a central portion of the sheet thickness and not less than 50 μm apart from one another and the arithmetic average of the measured values was determined as the average sharpness AS. The expression "central portion of the sheet thickness" may be any portion which is located about 1/4 or less of the sheet thickness from the center of the sheet thickness toward the obverse or reverse surface. Since the steel sheet for a can is a polycrystalline material, the average sharpness AS is a quantity from which the influence of the orientation of individual grains has been removed, enabling the sharpness to be correlated with the stress

corrosion cracking.

In order to more closely correlate the sharpness with the stress corrosion cracking, the present inventors adopted the relative average sharpness RAS. The relative average sharpness RAS is a value standardized by dividing the average sharpness AS of a material under test by the average sharpness AS of a standard sample free from work strain. The relative average sharpness RAS is a physical quantity for a steel sheet and can be determined using a scanning electron microscope and an image analyzer by reference to the above article (Journal of the Japan Institute of Metal, Vol. 55, No. 1 (1991) pp. 22-28).

According to experiments conducted by the present inventors, the relative average sharpness RAS shows a correlation with stress corrosion cracking. The upper limit of the relative average sharpness RAS is limited to 0.85 because if this value exceeds 0.85 the stress corrosion cracking cannot be completely prevented.

The sample applied to the ECP measurement is polished from one surface to the central portion of the sheet thickness and finished by chemical polishing to bring the surface to be exposed to an electron beam to a specular state.

The chemical composition of the steel of the present invention, that is, the function and proper percentage composition range of individual elements, will now be described.

C: When the C content exceeds 0.0015%, the stress corrosion cracking cannot be completely prevented. In addition, the earring property, DWI property, and flange forming property are deteriorated in the case of a very thin steel sheet for a two-piece can, and the flange forming property is deteriorated in the case of a very thin steel sheet for a welded can. For this reason, the C content is limited to not more than 0.0015%.

Although the mechanism of the influence of C on these properties has not been elucidated, it is believed as follows.

(1) Regarding the relationship between C and stress corrosion cracking, in order to completely prevent stress corrosion cracking, it is necessary to ensure a given amount of C in a solid solution form. When the C content exceeds the upper limit value, the number of precipitation sites of carbides becomes large, making it impossible to ensure C in a solid solution form useful for the prevention of stress corrosion cracking.

(2) The reason why the steel of the present invention exhibits an excellent earring property when applied to a very thin steel sheet for a two-piece can is that the C content of the steel of the present invention is so low that an increase in purity of the composition is significant, improving the aggregate structure governing the earring property.

(3) The reason why the steel of the present invention exhibits an excellent DWI property is that the C content of the steel of the present invention is so low that no carbide harder than ferrite is present and, therefore, when secondary cold rolling is carried out with the same reduction ratio as in the case of the conventional steel, the internally accumulated strain is smaller and the resistance to deformation at the time of DWI is lower.

(4) The reason why the steel of the present invention exhibits an excellent flange forming property when applied to a very thin steel sheet for a welded can is that the C content of the steel of the present invention is so low that such a weld hardening phenomenon as observed in the conventional steel does not occur, enabling the stress concentration on the hard spot to be avoided. Further, the C content of the steel of the present invention is so low that carbides detrimental to the ductility are absent. Therefore, even when secondary cold rolling is carried out, the steel exhibits high local ductility, indicating that the steel has high potential deformability in flanging.

When the production of a very thin steel sheet for a two-piece can and a very thin steel sheet for a welded can in a smaller sheet thickness is contemplated, the C content is preferably 0.0010% or less.

Mn: Mn should be present in an amount of not less than 0.05 % because when the Mn content is less than 0.05%, hot shortness occurs, making it impossible to prepare a steel sheet for a can. On the other hand, when the Mn content exceeds 0.40%, the steel sheet is excessively hardened to deteriorate flange forming property and DWI property and, at the same time, the composition purification effect attained by reduction in C content is reduced, causing the earring property to be deteriorated. Further, the cost is increased. For this reason, the Mn content is limited to 0.05 to 0.40%.

P: P is an element that need not be intentionally added. Specifically, it is an unavoidable impurity element that significantly hardens the steel. When the P content exceeds 0.06%, the steel sheet is excessively hardened, deteriorating the flange forming property and the DWI property. In addition, the composition purification effect attained by reduction in C content is reduced, causing the earring property to be deteriorated. Further, the corrosion resistance is deteriorated. For this reason, the upper limit of the P content is 0.06%. In order to provide better flange forming property, DWI property, earring property, and

corrosion resistance, it is preferred for the P content to be not more than 0.02%.

S: S is also an element that need not be intentionally added. Specifically, it is an unavoidable impurity element that increases the hot shortness. When the S content exceeds 0.06%, a sheet for a can cannot be produced due to hot shortness. For this reason, the upper limit of the S content is 0.06%. The S content is still preferably not more than 0.02%.

Al: Al is necessary as a deoxidizing element but need not be present as acid sol. Al. Further, when the relationship of Al with other steel ingredients is taken into consideration, the effect of the present invention is not lost when the acid sol. Al content is not more than 0.100%. When this content exceeds 0.100%, the Al_2O_3 inclusions are increased, causing flange cracking at the time of can making and deterioration in DWI property. Further, the cost is increased. For this reason, the upper limit of the acid sol. Al content is 0.100%.

N: N is also an element that need not be intentionally added. It is an unavoidable impurity element that hardens the steel. When the N content exceeds 0.0100%, the steel sheet is excessively hardened to deteriorate the flange forming property and the DWI property. In addition, the composition purification effect attained by reduction in C content is reduced, causing the earring property to be deteriorated. For this reason, the upper limit of the N content is 0.0100%.

B: The addition of B can further enhance the effect of the present invention. When the B content is lower than 0.0001%, the stress corrosion cracking is likely to occur. In addition, the earring property, DWI property, and neck forming property are deteriorated. For this reason, the lower limit of the B content is preferably 0.0001%. On the other hand, when the B content exceeds 0.0060%, the recrystallization temperature is increased and the alloy cost becomes excessively high. For this reason, the upper limit of the B content is preferably 0.0060%.

Ti and Nb: The addition of Ti and Nb can further enhance the effect of the present invention. When these elements are added in large amounts, the production of a very thin steel sheet, for a two-piece can, having an excellent earring property and a very thin steel sheet, for a welded can, having an excellent flange forming property can be facilitated. This, however, unfavorably makes it difficult to prevent stress corrosion cracking, incurs the alloy cost, and raises the recrystallization temperature. On the other hand, when the amount of these elements added is small, the production of a very thin steel sheet, for a two-piece can, having an excellent earring property and a very thin steel sheet, for a welded can, having an excellent flange forming property becomes difficult, although the problems of stress corrosion cracking, increased alloy cost, and raised recrystallization temperature can be avoided.

Accordingly, the present inventors have made detailed studies on the amounts of Ti and Nb added, while taking the relationship of these amounts with the other steel ingredients into consideration, which amounts can limit the increase in alloy cost and the rise in recrystallization temperature to a level acceptable from the viewpoint of industry and enable the production of a very thin steel sheet for a two-piece can, and a very thin steel sheet for a welded can, having high resistance to stress corrosion cracking. As a result, they have found that the limitation of the C content to the content range specified above in combination with the regulation of the amounts of these elements Ti and Nb added to the following amount ranges determined by taking the relationship between these amounts with the N content into consideration is useful for the above purpose.

Ti: When the Ti content, in relation to the N content, is below $3.4 \times ([\text{wt}\% \text{ of N}] - 0.0010)\%$, the earring property, DWI property, and neck forming property of the product are deteriorated. Therefore, the lower limit of the Ti content is $3.4 \times ([\text{wt}\% \text{ of N}] - 0.0010)\%$. On the other hand, when the Ti content exceeds 0.06%, it becomes difficult to completely prevent the stress corrosion cracking. In addition, the recrystallization temperature is remarkably increased, and the alloy cost becomes excessively high. For this reason, the upper limit of the Ti content is 0.06%.

Nb: When the Nb content, in relation to the N content, is below $6.6 \times ([\text{wt}\% \text{ of N}] - 0.0010)\%$, the earring property, DWI property, and neck forming property of the product are deteriorated. Therefore, the lower limit of the Nb content is $6.6 \times ([\text{wt}\% \text{ of N}] - 0.0010)\%$. On the other hand, when the Nb content exceeds 0.06%, it becomes difficult to completely prevent the stress corrosion cracking. In addition, the recrystallization temperature is remarkably increased, and the alloy cost becomes excessively high. For this reason, the upper limit of the Nb content is 0.06%.

Regarding Ti and Nb, the addition of any one of them in the amount range specified above is useful. However, the addition of these elements in combination are also possible.

In order to prevent stress corrosion cracking, C in a solid solution form and N in a solid solution form should be present in respective given amounts or more. For the regulation of the content of C in a solid solution form and the content of N in a solid solution form, it is preferred to accurately measure the amounts of C in a solid solution form and N in a solid solution form by an internal friction method, an

electric resistance method, or other methods. In the control of commercial products such as steel sheets for cans, the use of a simpler method is desired. According to the studies conducted by the present inventors, the above elements can be easily controlled by measuring the aging index without direct measurement of C in a solid solution form and N in a solid solution form.

5 The term "aging index" used herein refers to a difference between a flow stress when a tensile prestrain of 10% is applied to a tensile specimen and a lower yield stress after the above specimen is further subjected to artificial aging under conditions of 100 °C x one hr. When the aging index is below 15 MPa, it becomes difficult to completely prevent the stress corrosion cracking. Therefore, the lower limit of the aging index is limited to 15 MPa.

10 The process for producing a steel according to the present invention will now be described.

A steel produced by a conventional melt process is subjected to continuous casting or ingot making and slabbing to prepare a hot slab which is then hot-rolled. Prior to hot rolling, the slab may be heat-treated by any method commonly used in the art. Specifically, the hot slab may be directly hot-rolled or alternatively may be reheated in a heating furnace.

15 In the present invention, a hot rolling finishing temperature of 810 °C or above should be ensured. Therefore, the reheating cannot be carried out at such an excessively low reheating temperature as will make it impossible to ensure the finishing temperature in the hot rolling operation. In the case of conventional hot rolling equipment, when the reheating temperature is below 1000 °C, it becomes difficult to ensure the finishing temperature of 810 °C or above. For this reason, the reheating temperature is preferably 1000 °C or above.

20 When the hot rolling finishing temperature is below 810 °C, the object of the present invention cannot be attained for the following reason.

(1) The regulation of the sheet thickness of the hot-rolled steel strip becomes difficult, rendering the regulation of the sheet thickness in cold rolling difficult. This deteriorates the sheet thickness accuracy of the product steel sheet. In addition, the steel sheet is often broken during the cold rolling operation. This is a critical defect in the production of a very thin steel sheet.

(2) A texture detrimental to the earing property is formed in the hot-rolled steel strip, resulting in an increase in size of earing at the time of DWI of the product steel sheet. This deteriorates the yield of the material in a can manufacturer.

30 (3) It becomes difficult to completely prevent the stress corrosion cracking. This is also considered to derive from the formation of a texture in the hot-rolled steel strip.

When the final sheet thickness in hot rolling is less than 2.0 mm, it becomes difficult to ensure the required finishing temperature, which is unfavorable also from the viewpoint of preventing the stress corrosion cracking. For this reason, the lower limit of the final sheet thickness in hot rolling is 2.0 mm.

35 The studies conducted by the present inventors have revealed that the time taken from the emergence of a hot-rolled steel strip from a finishing final stand to the initiation of cooling of the hot-rolled steel strip on a run-out table (cooling initiation time) and the temperature at which the cooling is initiated (cooling initiation temperature) have an effect on the flange forming property and the relative average sharpness of ECP of the product steel sheet.

40 When the time taken from the emergence of a hot-rolled steel strip from a finishing final stand to the initiation of cooling of the hot-rolled steel strip on a run-out table (cooling initiation time) exceeds 1.5 sec, the flange forming property of the product steel sheet is deteriorated and, at the same time, the relative average sharpness of ECP becomes large. Therefore, this cooling initiation time should be limited to not more than 1.5 sec.

45 When the cooling initiation temperature is below [finishing temperature - 30] °C, the flange forming property of the product steel sheet is deteriorated and, at the same time, the relative average sharpness of ECP becomes large. Therefore, the cooling initiation temperature should be limited to [finishing temperature - 30] °C or above. Although the reason why these phenomena occur has not been fully elucidated yet, it is considered that a reduction in size of grains of the hot-rolled steel strip by the above limitations is involved in the above phenomena.

50 Regarding the coiling temperature of the hot-rolled steel strip, when the coiling temperature is above 720 °C, the amount of scale of the hot-rolled steel strip formed becomes excessively large, deteriorating the efficiency of the step of pickling. For this reason, the coiling temperature is preferably 720 °C or below.

55 After the completion of the hot rolling, the steel strip is subjected to a series of steps of pickling, cold rolling, and recrystallization annealing by conventional methods.

After the recrystallization annealing, the cold-rolled material is subjected to secondary cold rolling.

In the secondary cold rolling, when the average strain rate (SR) defined by the following equation (1) is less than 12.4 s⁻¹, the relative average sharpness of ECP becomes excessively large. Therefore, the lower

limit of the average strain rate is 12.4 s^{-1} .

$$5 \quad SR = \frac{1}{60 \sqrt{r}} \cdot \frac{1000}{\sqrt{R} \cdot \sqrt{t}} \ln \frac{1}{1-r} \quad \cdot \cdot \cdot (1)$$

wherein

- 10 r: reduction ratio, (-);
 R: radius of work roll, mm;
 t: sheet thickness on inlet side, mm; and
 v: peripheral speed of work roll, m/min.

15 When the reduction ratio (r) in secondary cold rolling is less than 0.7%, the stress corrosion cracking is likely to occur and, at the same time, the can strength becomes unsatisfactory. Therefore, the lower limit of the reduction ratio is 0.7%. On the other hand, when the reduction ratio exceeds 60%, the steel sheet is excessively hardened, causing the flange forming property and the DWI property to be deteriorated. For this reason, the upper limit of the reduction ratio is 60%.

20 The surface of the steel sheet of the present invention may be covered or coated by any method. Specifically, a good effect can be attained by applying any surface covering or coating commonly used in a steel sheet for a two-piece can and a steel sheet for a welded can, for example, plating such as tinning, nickel plating, and special substrate treatment followed by tinning at a very small coverage, or the application of a polymeric organic film.

A method for manufacturing a can using the steel of the present invention will now be described.

25 When the steel of the present invention is applied to a two-piece can, the can may be manufactured by any of DWI and multistage drawing. When the steel of the present invention is applied to a three-piece can, the can can be manufactured without limitation of blanking direction, that is, by any of a normal method (a method wherein blanking is carried out so that the rolling direction of the steel sheet is normal to the axial direction of the can barrel), a reverse method (a method wherein blanking is carried out so that the rolling direction of the steel sheet is parallel to the axial direction of the can barrel), and a method wherein the above blanking methods are combined. Further, the effect of the present invention can be attained also
 30 when the steel of the present invention is applied to a cemented can.

The present invention will now be described in more detail with reference to the following examples.

35 Example 1

40 Steels comprising chemical ingredients specified in Table 1 were prepared by the melt process in a converter, and slabs of these steels were cooled to room temperature, reheated to a slab reheating temperature in the range of from 1000 to 1290 °C and hot-rolled at a finishing temperature in the range of from 800 to 950 °C to a thickness of 3.0 mm. The resultant hot-rolled steel strips, 0.4 to 1.9 sec after the emergence from a finishing final stand, were started to be cooled on a run-out table, coiled, pickled, cold-rolled, continuously annealed, subjected to secondary cold rolling to a thickness of 0.17 mm, and finally plated with tin in a very small thickness.

45 The aging index, relative average sharpness in ECP, resistance to stress corrosion cracking, flange forming property, earring property, and paneling strength of the very thinly tinned steel sheets thus obtained are given in Table 2.

50 In Tables 1 and 2, sample Nos. 1 to 6 fall within the scope of the present invention, and sample Nos. 7 to 10 are comparative examples which are outside the scope of the present invention. For sample No. 7 which is outside the scope of the present invention, the chemical ingredients C and Ti, the aging index, and the relative average sharpness are outside the scope of the present invention. For sample No. 8, the sharpness is outside the scope of the present invention although the chemical ingredients fall within the scope of the present invention. For sample No. 9, the sharpness is outside the scope of the present invention. Further, sample No. 10, the chemical ingredient Ti and the aging index are outside the scope of the present invention.

55 In Tables 1 and 2, the numerical values outside the scope of the present invention are underlined. Further, "acceptable" evaluation results are expressed by O, while "unacceptable" evaluation results are expressed by X.

Evaluation for the results of property tests of each sample will now be described.

The resistance to stress corrosion cracking was evaluated in terms of the ratio E_1/E_0 wherein E_0 represents the elongation at break as measured by pulling a tensile specimen in the atmosphere at room temperature at a strain rate of 10^{-6} s^{-1} and E_1 represents the elongation at break as measured by pulling the specimen taken from used in the measurement of E_0 in a corrosion accelerating solution at the same strain rate at 80° C . When the ratio E_1/E_0 was not less than 0.90, the resistance to stress corrosion cracking was evaluated as "acceptable," while when it was less than 0.90, the resistance to stress corrosion cracking was evaluated as "unacceptable."

The flange forming property was evaluated in terms of the degree of forming to failure in a simulation of flanging of a welded can by means of a flange forming machine. When the degree of forming was not less than 9.0%, the flange forming property was evaluated as "acceptable," while when the degree of forming was less than 9.0%, the flange forming property was evaluated as "unacceptable."

The earring property was evaluated in terms of a percentage of a value determined by molding a cup using a drawer and dividing a difference between the average height of crests and the average height of roots of the earring by the average height of the roots. When the degree of earring was not more than 3.5%, the earring property was evaluated as "acceptable," while when it exceeded 3.5%, the earring property was evaluated as "unacceptable."

The paneling strength was evaluated as follows. A barrel of a can was first prepared by means of a wire seam welder, and a rubber liner was pressed against both ends of the barrel to temporarily seal the can. Then, the air within the can was gradually discharged by means of a vacuum pump to measure the difference between the external pressure and the internal pressure at a moment of the occurrence of paneling (depression of the barrel of the can by the external pressure). When the paneling strength was not less than 2.20 kg/cm^2 , the paneling strength was evaluated as "acceptable," while when it was less than 2.20 kg/cm^2 , the paneling strength was evaluated as "unacceptable."

Table 1

	Sample No.	Chemical ingredients (wt.%)							
		C	Mn	P	S	Sol.Al	N	B	Others
Inv.	1	0.0015	0.08	0.006	0.007	0.002	0.0011	0.0004	-
	2	0.0010	0.11	0.007	0.009	0.045	0.0052	0.0039	-
	3	0.0007	0.21	0.012	0.014	0.011	0.0015	0.0001	Nb:0.0038
	4	0.0008	0.21	0.014	0.012	0.037	0.0024	0.0004	Nb:0.0287
	5	0.0006	0.40	0.035	0.025	0.016	0.0021	0.0006	Ti:0.0039
	6	0.0005	0.30	0.033	0.026	0.095	0.0024	0.0014	Ti:0.0186
Out-side the inv.	7	<u>0.0016</u>	0.17	0.006	0.007	0.030	0.0066	-	<u>Ti:0.0635</u>
	8	0.0006	0.18	0.008	0.010	0.018	0.0021	0.0005	-
	9	0.0006	0.30	0.035	0.025	0.016	0.0021	-	Ti:0.0039
	10	0.0005	0.30	0.033	0.026	0.095	0.0024	0.0011	<u>Ti:0.0711</u>

Table 2

Sample No.	Aging index (MPa)	Relative average sharpness	Resistance to stress corrosion cracking	Flange working property	Earring property	Paneling strength	Overall evaluation
1	28	0.31	O	O	O	O	O
2	21	0.33	O	O	O	O	O
3	26	0.24	O	O	O	O	O
4	19	0.22	O	O	O	O	O
5	25	0.11	O	O	O	O	O
6	17	0.46	O	O	O	O	O
7	13	0.91	X	X	X	O	X
8	30	0.86	X	O	O	X	X
9	27	0.88	X	X	X	X	X
10	14	0.65	X	O	O	O	X
Inv.							
Out-side the inv.							

Example 2

Steels comprising chemical ingredients specified in Table 3 were prepared by the melt process in a converter, and hot rolling was carried out under production conditions specified in Table 4, i.e., finishing temperature, finishing sheet thickness, time taken from emergence of the hot-rolled steel strip from a

finishing final stand to the initiation of cooling thereof on a run-out table (cooling initiation time), cooling initiation temperature, and coiling temperature. Thereafter, the hot-rolled steel strips were pickled, cold-rolled, continuously annealed, subjected to secondary cold rolling under conditions of an average strain rate and a reduction ratio in secondary cold rolling specified in Table 4 to a thickness of 0.20 mm, and then

tinned. The aging index, relative average sharpness in ECP, resistance to stress corrosion cracking, flange forming property, earring property, and compressive strength of the tinned steel sheets thus obtained are also given in Table 4.

In Table 3, for sample Nos. 11 to 18, the chemical composition falls within the scope of the present invention, and sample Nos. 19 to 22 are comparative examples which are outside the scope of the present invention. For sample No. 19, the chemical ingredients C and Ti are outside the scope of the present invention; for sample No. 20, the chemical ingredients C, S, and N are outside the scope of the present invention; for sample No. 21, the chemical ingredients Mn, P, and sol. Al are outside the scope of the present invention; and for sample No. 22, the chemical ingredient Ti is outside the scope of the present invention.

As can be seen from Table 4, sample Nos. 19 to 22, production conditions are also outside the scope of the present invention. Specifically, for sample No. 19, the aging index is outside the scope of the present invention; for sample No. 20, the cooling initiation time, cooling initiation temperature, average strain rate, aging index, and relative average sharpness are outside the scope of the present invention; for sample No. 21, the hot rolling finishing temperature, average strain rate, secondary cold rolling reduction ratio, and sharpness are outside the scope of the present invention; and for sample No. 22, the average strain rate, secondary cold rolling reduction ratio, aging index, and sharpness are outside the scope of the present invention.

Tests and evaluation on properties of each sample will now be described.

The resistance to stress corrosion cracking was evaluated in the same manner as in Example 1.

The flange forming property was evaluated in terms of the degree of forming to failure in a test wherein, after an open end of a DWI can body is trimmed, the diameter of the open end is widened while inserting a conical punch into the open end by means of a flanging tester. When the degree of forming is not less than 9.0%, the flange forming property was evaluated as "acceptable," while when the degree of forming is less than 9.0%, the degree of forming was evaluated as "unacceptable."

The earring property was evaluated in the same manner as in Example 1.

The compressive strength was evaluated by preparing a can body of a steel sheet for a DWI can, subjecting the can body to heat treatment corresponding to drying of a coating in an atmosphere drier, sealing the opening of the can body with a rubber liner, and gradually introducing compressed air into the can body to determine a critical pressure which causes the can bottom to buckle. When the critical pressure was not less than 7.5 kgf/cm², the compressive strength was evaluated as "acceptable," while when it was less than 7.5 kgf/cm², the compressive strength was evaluated as "unacceptable."

In Tables 3 and 4, the numerical values outside the scope of the present invention are underlined. Further, "acceptable" evaluation results are expressed by O, while "unacceptable" evaluation results are expressed by X.

Table 3

	Sample No.	Chemical ingredients (wt.%)							
		C	Mn	P	S	Sol.Al	N	B	Others
Inv.	11	0.0009	0.12	0.005	0.005	0.031	0.0011	0.0003	-
	12	0.0007	0.22	0.016	0.015	0.014	0.0022	0.0036	-
	13	0.0006	0.24	0.018	0.012	0.027	0.0006	0.0002	Nb:0.0039
	14	0.0004	0.14	0.008	0.011	0.005	0.0086	0.0007	Nb:0.0294
	15	0.0010	0.18	0.007	0.008	0.025	0.0008	0.0006	Ti:0.0041
	16	0.0008	0.18	0.010	0.013	0.021	0.0046	0.0020	Ti:0.0223
	17	0.0006	0.19	0.009	0.011	0.018	0.0048	0.0005	Ti:0.0203
	18	0.0005	0.21	0.011	0.010	0.024	0.0037	0.0009	Ti:0.0229
Out-side the inv.	19	<u>0.0016</u>	0.17	0.006	0.007	0.030	0.0049	-	<u>Ti:0.0825</u>
	20	<u>0.0033</u>	0.25	0.014	<u>0.067</u>	0.008	<u>0.0127</u>	0.0012	-
	21	0.0007	<u>0.41</u>	<u>0.063</u>	0.011	<u>0.114</u>	0.0065	-	Ti:0.0045
	22	0.0009	0.12	0.005	0.005	0.031	0.0051	0.0008	<u>Ti:0.0607</u>

Table 4

	Sample No.	Production conditions						Test results						Overall evaluation
		Hot roll finishing temp. °C	Final sheet thickness mm	Cooling initiation time sec	Cooling initiation temp. °C	Hot rolling temp. °C	Average strain rate s ⁻¹	Reduction in secondary cold rolling %	Aging index (MPa)	Relative average sharpness	Resistance to stress corrosion cracking	Flange forming property	Earring property	
Inv.	11	879	3.0	0.8	862	351	347.4	12	36	0.52	○	○	○	○
	12	864	3.0	0.7	851	367	977.4	37	24	0.55	○	○	○	○
	13	901	3.0	1.1	879	675	1676.6	46	22	0.44	○	○	○	○
	14	815	2.4	0.4	851	473	1256.8	35	18	0.46	○	○	○	○
	15	911	3.0	1.1	890	612	555.9	35	24	0.30	○	○	○	○
	16	863	2.7	0.5	858	660	1622.7	35	25	0.62	○	○	○	○
	17	870	3.0	0.6	858	642	844.2	35	18	0.17	○	○	○	○
	18	906	3.0	0.6	894	336	630.1	35	19	0.19	○	○	○	○
Out-side the inv.	19	908	3.0	1.0	887	550	188.7	35	14	0.35	×	×	○	×
	20	891	3.0	1.7	858	476	12.0	35	13	0.89	×	×	○	×
	21	807	3.0	1.5	825	613	11.7	0.5	21	0.93	×	×	×	×
	22	893	3.0	1.2	866	619	12.2	65	13	0.98	×	×	○	×

55 Industrial Applicability

The present invention can be utilized in steel sheets for two-piece cans and steel sheets for three-piece cans, which steel sheets are thin, can ensure desired earring property, neck forming property, flange

forming property, and can strength, and further have high resistance to stress corrosion cracking.

Claims

- 5 1. A steel sheet, for a can, having high resistance to stress corrosion cracking, characterized by comprising, by weight,
 C: not more than 0.0015%, Mn: 0.05 to 0.40%, P: not more than 0.06%, S: not more than 0.06%,
 acid sol. Al: not more than 0.10%, and N: not more than 0.0100% with the balance consisting of iron
 and unavoidable impurities,
 10 said steel sheet having an aging index of not less than 15 MPa and a relative average sharpness of
 electron channelling patterns of not more than 0.85 as measured on 20 or more grains located in a
 central portion of the sheet thickness and not less than 50 μm apart from one another.
- 15 2. The steel sheet, for a can, having high resistance to stress corrosion cracking, according to claim 1,
 characterized by further comprising, in addition to the chemical ingredients described in claim 1, at
 least one member selected from Ti: not less than $3.4 \times ([\text{wt}\% \text{ of N}] - 0.0010)\%$ to not more than 0.06%
 and Nb: not less than $6.6 \times ([\text{wt}\% \text{ of N}] - 0.0010)\%$ to not more than 0.06%.
- 20 3. A process for producing a steel sheet, for a can, having high resistance to stress corrosion cracking,
 characterized by comprising the steps of:
 hot-rolling a hot steel slab comprising, by weight,
 C: not more than 0.0015%, Mn: 0.05 to 0.40%, P: not more than 0.06%, S: not more than 0.06%,
 acid sol. Al: not more than 0.10%, and N: not more than 0.0100%, with the balance consisting of iron
 and unavoidable impurities,
 25 at a finishing temperature of not less than 810°C to a thickness of not less than 2.0 mm, water-
 cooling the resultant hot-rolled steel strip on a run-out table within 1.5 sec or less after emergence from
 a finishing final stand of a hot rolling machine from a temperature of not less than [finishing temperature
 - 30]°C and subjecting the cooled steel strip to coiling, pickling, cold rolling, and recrystallization
 annealing; and
 30 subjecting the annealed steel strip to secondary cold rolling with a reduction ratio of 0.7 to 60% so
 that the average strain rate (SR) defined by the following equation (1) is not less than 12.4 sec^{-1} ,
 thereby preparing a steel sheet having an aging index of not less than 15 MPa and a relative
 average sharpness of an electron channelling pattern of not more than 0.85 as measured on 20 or more
 grains located in a central portion of the sheet thickness and not less than 50 μm apart from one
 35 another:

$$SR = \frac{1}{60 \sqrt{r}} \cdot \frac{1000}{\sqrt{R}} \cdot \frac{v}{\sqrt{t}} \ln \frac{1}{1-r} \quad \cdot \cdot \cdot (1)$$

40

wherein

- r: reduction ratio, -;
 R: radius of work roll, mm;
 45 t: sheet thickness on inlet side, mm; and
 v: peripheral speed of work roll, m/min.

- 50 4. The process for producing a steel sheet, for a can, having high resistance to stress corrosion cracking
 according to claim 3, characterized in that said steel further comprises, in addition to the chemical
 ingredients described in claim 3, at least one member selected from Ti: not less than $3.4 \times ([\text{wt}\% \text{ of N}] - 0.0010)\%$
 to not more than 0.06% and Nb: not less than $6.6 \times ([\text{wt}\% \text{ of N}] - 0.0010)\%$ to not more
 than 0.06%.

55

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP94/01226

A. CLASSIFICATION OF SUBJECT MATTER		
Int. Cl ⁶ C22C38/06, 38/14, C21D8/04, 9/48		
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)		
Int. Cl ⁵ C22C38/00-38/16, C21D8/00-8/04, 9/46-9/48		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
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.
A	JP, A, 5-117807 (Kawasaki Steel Corp.), May 14, 1993 (14. 05. 93), Lines 2 to 11, column 1, line 13, column 3 to line 11, column 10, (Family: none)	1-4
A	JP, A, 3-285046 (Kawasaki Steel Corp.), December 16, 1991 (16. 12. 91), Page 1, table 2 of page 6, (Family: none)	1-4
A	JP, A, 1-306527 (Toyo Kohan K.K.), December 11, 1989 (11. 12. 89), Lower left column to line 3, lower right column, page 1, (Family: none)	1-4
A	JP, A, 63-203721 (Kobe Steel, Ltd.), August 23, 1988 (23. 08. 88), Page 1 to line 5, upper left column, page 2, (Family: none)	1-4
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "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) "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 "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 "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 "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 "&" document member of the same patent family		
Date of the actual completion of the international search		Date of mailing of the international search report
September 28, 1994 (28. 09. 94)		October 11, 1994 (11. 10. 94)
Name and mailing address of the ISA/ Japanese Patent Office		Authorized officer
Facsimile No.		Telephone No.