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METHOD OF PRODUCING NON-AGEING SPECIAL LOW CARBON IRON SHEETS

Kameo Matsukura, Yawata, and Morihiko Yazu, Tobata,
Japan, assignors to Yawata Iron & Steel Co., Ltd.,
Tokyo, Japan, a corporation of Japan

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This invention relates to a method of producing non-ageing special low carbon iron sheets which are very high in cold-workability and enamelability.

Much study has been done, recently, relative to the production of once enameled special low carbon iron sheets which can be once enameled in white or a bright color. However, no favorable results have been obtained on the cold-workability and many problems have been caused on the cold-shaping of special low carbon iron plates.

Pure iron sheets of low carbon content have been used for enameling with a view to preventing various defects, such as fish-scaling, blow holes, warping and sagging after enameling. However, in such material, the oxygen content increases inversely proportionally to the carbon content, the steel itself is likely to be stained with non-metallic impurities and is low in cold-shapeability. Further, due to nitrogen contained in such iron sheet, the material will age, its mechanical properties or, specifically, its cold-workability will deteriorate with the lapse of time and strain patterns impairing the appearance will be produced in shaping. In such case, if an alloying ingredient forming a carbide, such as titanium is used, the carbon in the special low carbon iron sheet will be able to be fixed but the cost will be high and, additionally, if titanium corresponding to the carbon content is retained, the material will become so hard that the cold-shapeability will be greatly impaired. From this viewpoint, when the carbon content is reduced, the oxygen content in the molten steel will increase in inverse proportion to the carbon content and the material will thus deteriorate.

The adhesion of the enameled product is most important in once enameling in white or a bright color. In the conventional method an adhesion increasing substance, such as cobalt oxide, is used as a ground coat having a high adhesiveness when a plurality of bakings is carried out in each enameling. A grayish black ground coat is coated with a white or bright colored cover coat by enameling one or more times. Today, in enameling once, in order to obtain satisfactory adhesion, some surface treatment is usually required before enameling. Further, it is often required in shortening the process to once apply glassy enameling in white or a bright color without using any ground coat.

The surface treating process to increase adhesion is to roughen the surface of the material plate by a mechanical means or chemical etching, to apply a thin layer of a metal which increases adhesiveness, e.g. nickel or cobalt, to the surface of the material plate or both of these treatments.

When any material is enameled once, phenomena such as peeling and fish-scaling are likely to occur. It is one of the objects of the present invention to produce an iron material having no such tendency. Thus the present invention is useful as a cover coating slip containing no such adhesion increasing oxide as nickel, cobalt, antimony or molybdenum.

An object of the present invention is to provide non-ageing special low carbon iron sheets in which the above mentioned points are improved and which are high in cold-shapeability.

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Generally, in producing iron sheets or steel sheets to be enameled, a steel is first made, is made an ingot, is then heated in a uniformly heating furnace, is hot-rolled to an intermediate thickness, is pickled, is then singly or continuously cold-rolled, is softened and recrystallized and is brightly annealed.

The material for the special low carbon iron sheet produced according to the present invention may first have a carbon content of at least 0.02%. In such case, a material having a higher carbon content may be used, but 0.040 to 0.070% C is most preferable because, inter alia, the oxygen content in the steel will increase in inverse proportion to the carbon content in the steel. For example, according to measured results, the relation between carbon content and oxygen content is as follows: 0.015% O₂ for 0.08% C, 0.02% O₂ for 0.07% C, 0.026% O₂ for 0.06% C, 0.038% O₂ for 0.05% C, 0.07% O₂ for 0.04% C, and more than 0.100% O₂ for 0.03% C, respectively. Due to this increased content of oxygen, aluminum, vanadium, boron or the like which are added to form a nitride for non-ageing will be, for the most part, consumed and deterioration of the quality of steel by the non-metallic impurities will result. Secondly, if the carbon content is higher than is specified, the decarburization will take much longer when the annealing is carried out in the subsequent step for preventing surface flaws after enameling.

Additionally, the maximum manganese content should be 0.20%. Usually, in order to prevent red-heat brittleness when hot-rolling a steel material, more than 0.30% manganese is contained in the material. However, such a large manganese content is likely to cause sagging when the steel material to be enameled is baked. The red-heat brittleness can be prevented by, e.g., delaying the hot-rolling and adjusting the thickness of the hot-rolled heat sheet. In conclusion, a material having a manganese content of less than 0.20% is favorable in enamel baking. The most preferable is a content of less than 0.05% Mn.

Moreover, a nitride producing element must be present for the purpose of eliminating solid-soluble nitrogen which causes ageing of the product. The material must also contain an element which is 0.020 to 0.080% acid-soluble aluminum, or 0.003 to 0.020% acid-soluble boron, or 0.020 to 0.050% acid-soluble vanadium or two or three of them and which will form a stable nitride by annealing. According to the results of many tests, the nitrogen content in such material is 0.0015 to 0.0070% (usually 0.0030%). In order that such nitrogen may be deposited as a stable nitride and the product may be made non-ageing, the above mentioned nitride producing agent must be added.

With the above mentioned 0.020 to 0.080% acid-soluble Al, the product will be a killed steel. When a slight amount of Al or that much of B or V is added, rimming action will not be prevented and the resulting product is a rimmed steel.

The smaller the amount of such unavoidably accompanying elements as P, S or Cu, the better. However, their content can be about the same as in current cold-rolled steel sheets.

The hot-rolling may be conducted by any method. Usually a continuous rolling mill is used today, but the present invention is not limited to such a method. From the viewpoint that the material can be easily made to the required final thickness in the cold-rolling step following pickling, it may be made to be 2.0 to 4.5 mm. thick in the hot-rolling. In view of the fact that, in a killed steel containing aluminum, the nitride is deposited in the subsequent annealing step and, in a hot-rolled sheet, the deposition is limited to less than 10%, it is necessary to increase the cooling speed.

In an Al killed steel of the same composition, when

the nitride is deposited during annealing, the cold-shapeability of the product of elongated crystal grains will be higher than that of equal axis crystal grains. Of course, in rimmed steel, the same is also true.

The cold-rolling can be conducted with many passes such a continuously operating tandem strip mill or reversing cold mill. The rate of depression is not critical and can be determined by the crystal granularity and hot-rolled thickness to obtain a proper cold-shapeability and the thickness of the product and is usually more than 30%. Prior to annealing after cold-rolling, the material may be or may not be pressed through an electric cleaning step.

Annealing is a treatment to improve the mechanical properties, non-ageing and enamelability following the cold-rolling and is a final step in the process for making the non-ageing special low carbon iron sheet material by the present invention.

In this final step, such additional treatment, combined with the normal recrystallizing softening annealing, as a decarburizing and denitrifying treatment is carried out. This treatment is a batch or continuous heat-treatment which is carried out in such a manner that the carbon in the steel is oxidized but the iron is not oxidized, that is, at a temperature of 620 to 900° C. in an atmosphere containing less than 30% by volume water vapor. The atmosphere to be used therein may be composed of water vapor and a mixture of hydrogen, nitrogen and any other gases which are inert and will not oxidize or cement the iron at said temperature. Decomposed ammonia, HNX gas and DX gas are examples of the gas containing hydrogen. The carbon content in the product will be reduced by this annealing to a value not larger than 0.020%. The most preferable is not more than 0.010% C. By the above annealing step, the nitrogen in the sheet will be deposited as a stable nitride such as AlN, BN or VN and the solid-soluble nitrogen will be removed. If carbon is reduced by annealing, the product will be able to be decarburized without increasing the oxygen content. The mechanical and chemical roughening of the surface in order to further improve the adhesiveness of once enameling can be carried out in the cold-rolling or in any subsequent step.

Thus the special low carbon iron sheet produced according to the present invention is as follows:

(1) In making the material steel, it is composed of at least 0.02% carbon (most preferably 0.04 to 0.07% C), not more than 0.20% manganese (most preferably not more than 0.05% Mn) and 0.020 to 0.080% acid-soluble aluminum, 0.003 to 0.020% boron or 0.020 to 0.050% vanadium or a compound of these and is characterized mostly by containing an alloying element forming a stable nitride. In the case of a killed steel, the contained nitrogen will be substantially fixed as a nitride and therefore the total amount of nitrogen in the final product will be only slightly reduced. But, in the case of a rimmed steel, the amount of the fixed solid soluble nitrogen will be so small that a considerable amount of the other solid-soluble nitrogen than will form a nitride will be removed. According to an internal friction measuring method, in either case, the solid-soluble nitrogen in the product will not be more than 0.0002% which is said to be a value necessary for non-ageing.

(2) The steel ingot made of this composition is heated, is slabbed, is then treated on the surface and is hot-rolled to an intermediate thickness. In the hot-rolling or strip-rolling, this material will show hot-brittleness in the range of 930 to 1050° C. Therefore, the material is rolled by avoiding such temperatures. That is to say, it is roughly rolled at a temperature above 1050° C. It is then left to stand on a delay table until its temperature falls. Then it is finish-rolled below the brittleness temperature range, is water-cooled, wound up and pickled and is cold-rolled in a cold-rolling factory. From the standpoint of crystal granularity, a cold-rolling of at least 30% is preferable.

As a proper hot-rolling finishing temperature is secured by the delay before the hot-rolling mill, the cold-rolling rate will become higher but the subsequent steps will never be obstructed.

(3) Such cold-rolled sheet or coil is (or need not be) electrically cleaned and is then annealed so that carbon may be removed.

This annealing is the second feature of the method of producing non-ageing enamelable iron sheets having a low of carbon, oxygen and manganese and not having defects such as fish-scaling, bubbling, warping and curving.

This annealing may be conducted by any method. However, from the standpoint of heating or cooling speed, decarburizing speed and homogeneity of the material, it is most desirable to carry out the annealing in the form of a loose coil or open coil or continuously.

After the above mentioned annealing, the carbon content in the special low carbon iron sheet of the present invention will be 0.02% (most preferably not more than 0.010% C). That is to say, the composition of the special low carbon iron sheet as a product is as follows: C is not more than 0.02% and Mn is not more than 0.20%. The nitrogen in the rest except the normal impure metallic composition and iron will combine with the added aluminum, boron or vanadium to form a stable nitride, the amount of the solid-soluble nitrogen will be so small and the carbon content will also be low so that the product will be non-ageing and the oxygen content will be small in proportion to the carbon content in the time of making the steel and making it into an ingot. Thus, as compared with any existing enamelable iron sheet, the special low carbon iron sheet produced by the method of the present invention has the following characteristics: (a) the carbon content is lower, (b) the manganese content is lower, (c) the oxygen content is lower and (d) the solid soluble nitrogen content is much lower. Therefore, in enameling, it has the following features: (A) no defects such as fish-scaling, bubbling, warping and curving, (B) its cold-workability is high and (C) it is non-ageing. Though the above mentioned explanation has been detailed for enameling, the product is so high in cold-workability and is so non-ageing that it is cold-press-shaped. It is evident from the nature of the present invention that the product can be not only enameled but also painted.

Example 1

A hot-rolled steel material composed of 0.044% C, 0.017% Si, 0.18% Mn, 0.015% P, 0.018% S, 0.008% O₂, 0.032% Sol. Al and 0.0057% total N₂ was pickled, was cold-rolled at a rate of depression of 55%, was electrically cleaned and was then annealed at 700° C. for 5 hours in a wet hydrogen atmosphere of 15.5% by volume. The thus produced steel sheet had a composition of 0.003% C, 0.017% Si, 0.18% Mn, 0.015% P, 0.018% S, 0.010% O₂, 0.032% Sol. Al and 0.0055% total N₂ (the solid-soluble nitrogen by the internal friction method was 0.000008%).

The mechanical properties of the product obtained by the above mentioned treatment were as follows:

Thickness	-----mm.	1.00
Yielding strength	-----kg./mm. ²	16.3
Tensile strength	-----kg./mm. ²	30.1
Elongation	-----percent	48.8
Erichsen value	-----mm.	11.8
Hardness	-----	¹ 37.8

¹ Rockwell B scale.

Example 2

When a hot-rolled material composed of 0.054% C, 0.010% Si, 0.20% Mn, 0.014% P, 0.017% S, 0.021% O₂, 0.049% Sol. V and 0.043% total N₂ was cold-rolled and annealed under the same condition as in the above

Example 1, the obtained product steel sheet was of a composition of 0.004% C, 0.010% Si, 0.20% Mn, 0.014% P, 0.017% S, 0.021% O₂, 0.048% Sol. V and 0.0018% total N₂ (the solid-soluble nitrogen by the internal friction method was 0.000006%).

The mechanical properties of the above mentioned product were as follows:

Thickness	mm.	1.00
Yielding strength	kg./mm. ²	17.1
Tensile strength	kg./mm. ²	31.5
Elongation	percent	47.5
Erichsen value	mm.	11.5
Hardness		¹ 38.2

¹ Rockwell B scale.

The enamel adhesiveness of the product was shown to be higher than of any existing enamelable pure iron in the enamelability test, Du Pont type impact test, bending test and twisting test.

What we claim is:

1. In a method for producing non-ageing low carbon steel sheet which is superior to cold-workability and enamelability and which contains quantities of aluminum, boron, vanadium and manganese, the improvement comprising

(1) forming steel ingots containing acid-soluble Al of from 0.020 to 0.080%, acid-soluble boron of from 0.003 to 0.020% and acid-soluble vanadium of from 0.020 to 0.050% as nitride-producing elements, and further containing carbon of from 0.040 to 0.070% and manganese of below 0.20%,

(2) subjecting said ingot to slabbing,

(3) hot-rolling the resilient slab at a temperature above 1050° C. to a sheet of from 2.0 to 4.5 mm. in thickness,

(4) cold-rolling said sheet at the reduction rate above 30%, and

(5) subjecting said cold-rolled sheet to a decarburizing annealing at a temperature of from 620° to 900° C. in an atmosphere containing water vapor less than 30% by volume, thereby reducing the carbon content to less than 0.020% and reducing solid-soluble nitrogen content to less than 0.0002%.

2. Method of claim 1 wherein the nitride-producing element is a compound of at least two metals selected from the group consisting of aluminum, boron and vanadium.

3. Method of claim 1 wherein the nitride-producing element is one of the elements aluminum, boron and vanadium in its aforesated proportion.

4. Process of claim 1 wherein the final carbon content is less than 0.010%.

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DAVID L. RECK, *Primary Examiner*.

RAY K. WINDHAM, *Examiner*.

W. B. NOLL, H. F. SAITO, *Assistant Examiners*.