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ABSTRACT

Provided is a surface treated steel sheet for manufacturing a pipe having corrosion resistance against fuel vapor of fuel such as gasoline, light oil, bioethanol or bio-diesel fuel, and a pipe and a fuel supply pipe which use the steel sheet. In the surface treated steel sheet for manufacturing a pipe, a layer containing Zn, Co and Mo is formed on a surface of a steel sheet thus having corrosion resistance against fuel vapor. In the pipe, a layer containing Zn, Co and Mo is formed on an inner surface of the pipe formed of a steel sheet thus having corrosion resistance against fuel vapor. In the fuel supply pipe 20 which is formed of a steel sheet for supplying fuel to a fuel tank 23, the fuel supply pipe includes: a large-diameter pipe portion 21 through which the fuel passes; and a small-diameter pipe portion 22 which makes an upper portion of the large-diameter pipe portion and a lower portion of the large-diameter pipe portion communicate with each other for ventilation, and a layer containing Zn, Co and Mo having a plating thickness of 1.0 to 8.0μm is formed on an inner surface of the fuel supply pipe portion.

Claims :

1. A surface treated steel sheet for manufacturing a pipe, wherein a layer containing Zn, Co and Mo is formed on at least one surface of a steel sheet thus having corrosion resistance against fuel vapor.

2. The surface treated steel sheet for manufacturing a pipe according to claim 1, wherein a Ni layer is formed between the layer containing Zn, Co and Mo and the steel sheet.

3. The surface treated steel sheet for manufacturing a pipe according to claim 1, wherein a Fe-Ni diffusion layer is formed below the layer containing Zn, Co and Mo.

4. The surface treated steel sheet for manufacturing a pipe according to claim 1, wherein a Fe-Ni diffusion layer and a softened Ni layer are sequentially formed below the layer containing Zn, Co and Mo.

5. The surface treated steel sheet for manufacturing a pipe according to any one of claims 1 to 4, wherein a thickness of the layer containing Zn, Co and Mo is set to a value which falls within a range of 1.0 to 8.0μm.

6. The surface treated steel sheet for manufacturing a pipe according to any one of claims 1 to 5, wherein the fuel is gasoline, light oil, bioethanol or bio-diesel fuel.

7. A pipe, wherein a layer containing Zn, Co and Mo is formed on an inner surface of a pipe formed of a steel sheet thus having corrosion resistance against fuel vapor.

8. The pipe according to claim 7, wherein a Ni layer is

formed between the layer containing Zn, Co and Mo and the steel sheet.

9. The pipe according to claim 7, wherein a Fe-Ni diffusion layer is formed below the layer containing Zn, Co and Mo.

10. The pipe according to claim 7, wherein a Fe-Ni diffusion layer and a softened Ni layer are sequentially formed below the layer containing Zn, Co and Mo.

11. The pipe according to any one of claims 7 to 10, wherein a thickness of the layer containing Zn, Co and Mo is set to a value which falls within a range of 1.0 to 8.0μm.

12. The pipe according to any one of claims 7 to 11, wherein the fuel is gasoline, light oil, bioethanol or bio-diesel fuel.

13. A fuel supply pipe which is formed of a steel sheet for supplying fuel to a fuel tank, the fuel supply pipe comprising:

a large-diameter pipe portion through which the fuel passes; and

a small-diameter pipe portion which makes an upper portion of the large-diameter pipe portion and a lower portion of the large-diameter pipe portion communicate with each other for ventilation, and

a layer containing Zn, Co and Mo having a thickness of 1.0 to 8.0μm is formed on an inner surface of at least the small-diameter pipe portion thus having corrosion resistance against fuel vapor.

14. The fuel supply pipe according to claim 13, wherein a Ni layer is formed between the layer containing Zn, Co and Mo and the steel sheet.

15. The fuel supply pipe according to claim 13, wherein a Fe-Ni diffusion layer and a softened Ni layer are sequentially formed below the layer containing Zn, Co and Mo.

16. The fuel supply pipe according to any one of claims 13 to 15, wherein a thickness of the layer containing Zn, Co and Mo is set to a value which falls within a range of 1.0 to 8.0μm.

17. The fuel supply pipe according to any one of claims 13 to 16, wherein the fuel is gasoline, light oil, bioethanol or bio-diesel fuel.

Dated this 03/04/2012

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TOYO KOHAN CO., LTD.

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Fig. 1

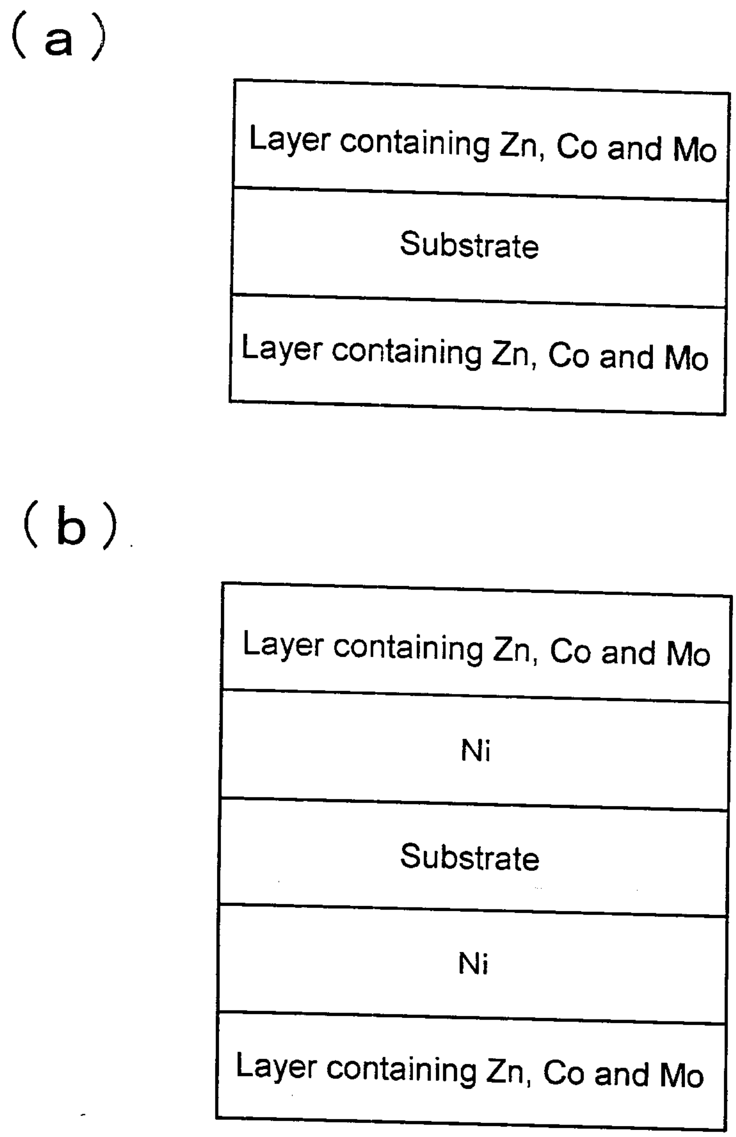

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Fig. 2

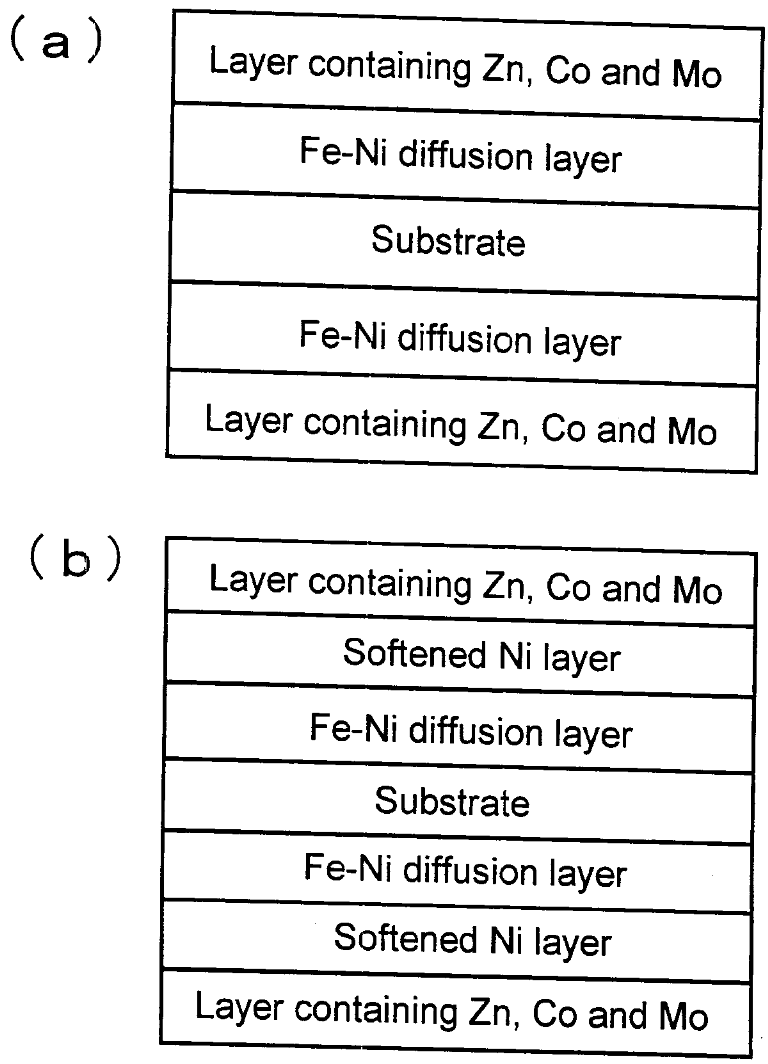

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Fig. 3

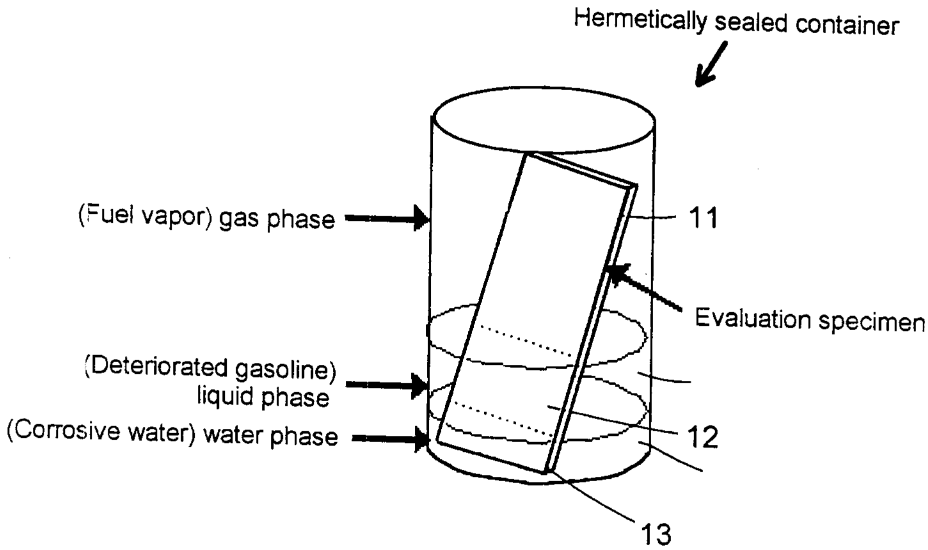

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Fig. 4

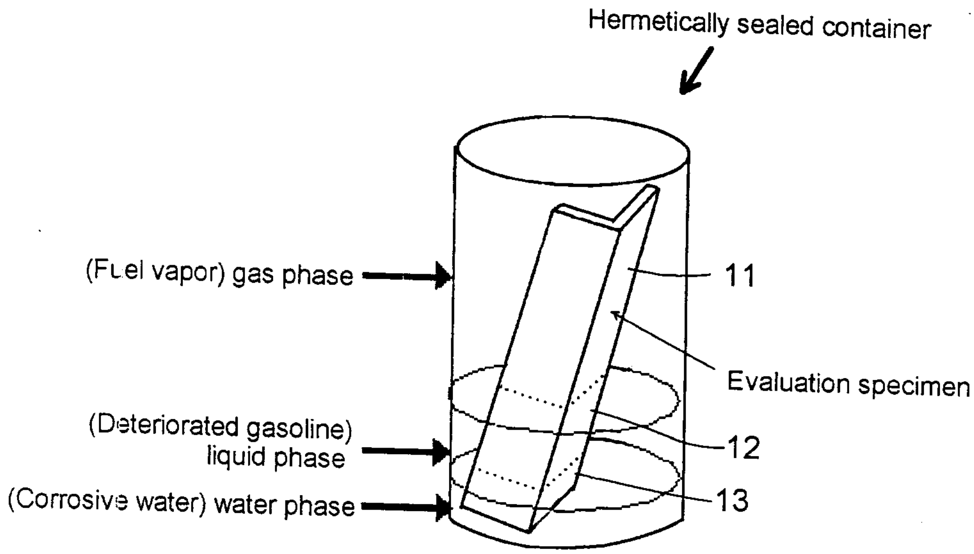

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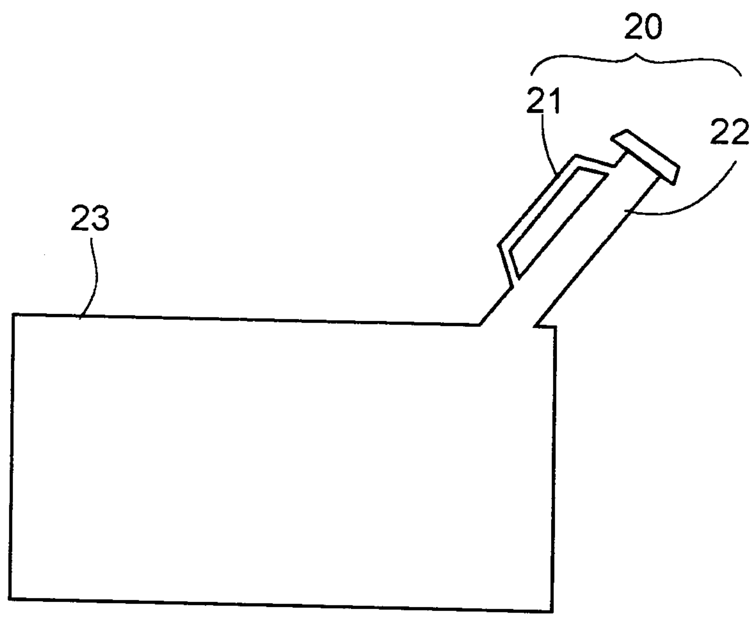
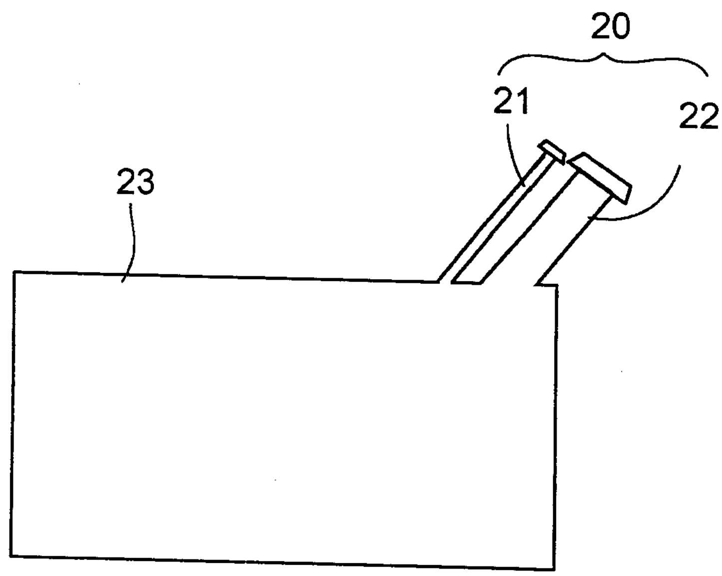
Fig. 5

(a)



(b)



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Description

Title of the Invention

SURFACE TREATED STEEL SHEET FOR MANUFACTURING PIPE HAVING CORROSION RESISTANCE AGAINST FUEL VAPORS, PIPE WHICH USES THE STEEL SHEET, AND FUEL SUPPLY PIPE WHICH USES THE STEEL SHEET

Technical Field

[0001]

The present invention relates to a surface treated steel sheet having corrosion resistance against fuel vapors, a pipe which uses the steel sheet, and a fuel supply pipe which uses the steel sheet.

Background Art

[0002]

Recently, for reducing a greenhouse effect gas, the movement toward the use of so-called bioethanol mixed gasoline produced by mixing bioethanol which is considered neutral to carbon into gasoline has been advancing steadily. However, when ethanol is added to gasoline, gasoline is liable to absorb moisture and hence, there is a possibility that water is mixed into gasoline in a fuel tank.

Further, when ethanol mixed gasoline is left for a long period, gasoline is deteriorated and an organic acid is formed in gasoline.

In this manner, when a moisture absorbed state and the deterioration of gasoline take place, ethanol can be mixed into both water and gasoline and hence, there arises a state where both water and an organic acid are contained in gasoline whereby there may be a case where the mixture of water and an organic acid is vaporized from a surface of gasoline. In such a case, an inner surface of a pipe which usually contacts with only gasoline vapor which substantially has no corrosiveness is exposed to a strong corrosive environment.

Accordingly, a pipe which is placed in an atmosphere of bioethanol mixed gasoline is required to possess corrosion resistance which is determined by taking into account such a corrosive environment.

To cope with such a corrosive environment, for example, patent document 1 discloses a fuel container for an automobile which has excellent corrosion resistance. The fuel container is manufactured such that a chromate film having a coating weight of ≤ 100 mg/m^2 expressed in terms of Cr and comprising an chromic acid, silica, an inorganic phosphoric acid and an organic phosphoric acid is applied to a surface of a steel sheet on which a Sn-Zn alloy plating having a coating weight of 10-70 g/m^2 and a Zn content of 1-50% in the alloy is formed, or, as the additional treatment, a resin-chromate film containing an organic resin is applied to the chromate film, and flange parts of a pair of bowl-shaped formed bodies having flanges are formed into an integral body by seam welding.

Prior Art Document

Patent Document

[0003]

Patent document 1: JP-A-2000-17450

Summary of the Invention

Problems that the Invention is to Solve

[0004]

However, with respect to a raw material used for manufacturing the fuel container for an automobile disclosed in the above-mentioned patent document 1, the required corrosion resistance in patent document 1 is the corrosion resistance of the raw material of a part of a fuel tank or the like which is immersed in automobile-use fuel such as gasoline and directly contacts with automobile-use fuel, but is not the corrosion resistance of the raw material against vapor of the automobile-use fuel.

For example, with respect to a pipe which is connected to a fuel tank such as a fuel supply pipe, as an actual use environment, the number of cases where the pipe is exposed to highly volatile vapor of automobile-use fuel is overwhelmingly larger than the number of cases where the pipe is directly exposed to automobile-use fuel.

Internationally, the problem on exhaustion of fossil fuels has been becoming seriously, and the use of bioethanol, bio-diesel fuel and the like has been spreading.

In this manner, in addition to gasoline which has been the conventional automobile fuel, there has been a demand for a raw material having sufficient properties against bioethanol, bio-diesel fuel and vapors of gasoline, bioethanol, bio-diesel fuel and the like.

Accordingly, the present invention has been made to overcome the above-mentioned conventional drawbacks, and it is an object of the present invention to provide a surface treated steel sheet for manufacturing a pipe having sufficient corrosion resistance against fuel, particularly, fuel vapor of fuel such as gasoline, light oil (diesel oil), bioethanol or bio-diesel fuel.

Further, it is another object of the present invention to provide a pipe which uses the surface treated steel sheet and a fuel supply pipe which uses the surface treated steel sheet.

Means for Solving the Problems

[0005]

(1) A surface treated steel sheet for manufacturing a pipe according to the present invention is characterized in that a layer containing Zn, Co and Mo is formed on at least one surface of a steel sheet thus having corrosion resistance against fuel vapor.

(2) The surface treated steel sheet for manufacturing a pipe according to the present invention is, in the above-mentioned constitution (1), characterized in that a Ni layer is formed between the layer containing Zn, Co and Mo and the steel sheet.

(3) The surface treated steel sheet for manufacturing a pipe according to the present invention is, in the

above-mentioned constitution (1), characterized in that a Fe-Ni diffusion layer is formed below the layer containing Zn, Co and Mo.

(4) The surface treated steel sheet for manufacturing a pipe according to the present invention is, in the above-mentioned constitution (1), characterized in that a Fe-Ni diffusion layer and a softened Ni layer are sequentially formed below the layer containing Zn, Co and Mo.

(5) The surface treated steel sheet for manufacturing a pipe according to the present invention is, in any one of the above-mentioned constitutions (1) to (4), characterized in that a thickness of the layer containing Zn, Co and Mo is set to a value which falls within a range of 1.0 to 8.0μm.

(6) The surface treated steel sheet for manufacturing a pipe according to the present invention is, in any one of the above-mentioned constitutions (1) to (5), characterized in that the fuel is gasoline, light oil, bioethanol or bio-diesel fuel.

(7) A pipe according to the present invention is characterized in that a layer containing Zn, Co and Mo is formed on an inner surface of a pipe formed of a steel sheet thus having corrosion resistance against fuel vapor.

(8) The pipe according to the present invention is, in the above-mentioned constitution (7), characterized in that a Ni layer is formed between the layer containing Zn, Co and Mo and the steel sheet.

(9) The pipe according to the present invention is, in the above-mentioned constitution (7), characterized in that a

Fe-Ni diffusion layer is formed below the layer containing Zn, Co and Mo.

(10) The pipe according to the present invention is, in the above-mentioned constitution (7), characterized in that a Fe-Ni diffusion layer and a softened Ni layer are sequentially formed below the layer containing Zn, Co and Mo.

(11) The pipe according to the present invention is, in any one of the above-mentioned constitutions (7) to (10), characterized in that a thickness of the layer containing Zn, Co and Mo is set to a value which falls within a range of 1.0 to 8.0μm.

(12) The pipe according to the present invention is, in any one of the above-mentioned constitutions (7) to (11), characterized in that the fuel is gasoline, light oil, bioethanol or bio-diesel fuel.

(13) A fuel supply pipe according to the present invention is characterized in that the fuel supply pipe is formed of a steel sheet for supplying fuel to a fuel tank, and includes:

a large-diameter pipe (main pipe) portion through which the fuel passes; and

a small-diameter pipe (breather pipe) portion which makes an upper portion of the large-diameter pipe portion and a lower portion of the large-diameter pipe portion communicate with each other for ventilation, and

a layer containing Zn, Co and Mo having a thickness of 1.0 to 8.0μm is formed on an inner surface of at least the small-diameter pipe portion thus having corrosion resistance against fuel vapor.

(14) The fuel supply pipe according to the present invention is, in the above-mentioned constitution (13), characterized in that a Ni layer is formed between the layer containing Zn, Co and Mo and the steel sheet.

(15) The fuel supply pipe according to the present invention is, in the above-mentioned constitution (13), characterized in that a Fe-Ni diffusion layer and a softened Ni layer are sequentially formed below the layer containing Zn, Co and Mo.

(16) The fuel supply pipe according to the present invention is, in any one of the above-mentioned constitutions (13) to (15), characterized in that a thickness of the layer containing Zn, Co and Mo is set to a value which falls within a range of 1.0 to 8.0μm.

(17) The fuel supply pipe according to the present invention is, in any one of the above-mentioned constitutions (13) to (16), characterized in that the fuel is gasoline, light oil, bioethanol or bio-diesel fuel.

Advantageous Effects of the Invention

[0006]

The surface treated steel sheet for manufacturing a pipe according to the present invention, the pipe which use the surface treated steel sheet according to the present invention, and the fuel supply pipe which uses the surface treated steel sheet according to the present invention can suppress the generation of rust even when they are exposed to fuel vapor of automobile-use fuel such as gasoline, light oil, bioethanol or bio-diesel fuel.

Brief Explanation of Drawings

[0007]

Fig. 1 is a schematic explanatory view showing the constitution of a surface treated steel sheet according to an embodiment 1 of the present invention, wherein (a) shows the constitution of the surface treated steel sheet where a layer containing Zn, Co and Mo is formed on both surfaces of the steel sheet which constitutes a substrate, and (b) shows the constitution of the surface treated steel sheet where a Ni layer is firstly applied to both surfaces of the steel sheet which constitutes a substrate, and a layer containing Zn, Co and Mo is formed on the Ni layer.

Fig. 2 is a schematic explanatory view showing the constitution of a surface treated steel sheet according to an embodiment 2 of the present invention, wherein (a) shows the constitution of the surface treated steel sheet where a layer containing Zn, Co and Mo and a Fe-Ni diffusion layer are formed on both surfaces of a steel sheet which constitutes a substrate with the Fe-Ni diffusion layer arranged inside the layer containing Zn, Co and Mo, and (b) shows the constitution of the surface treated steel sheet where a layer containing Zn, Co and Mo, a Fe-Ni diffusion layer and a softened Ni layer are formed on both surfaces of a steel sheet which constitutes a substrate with the Fe-Ni diffusion layer arranged inside the layer containing Zn, Co and Mo and with the softened Ni layer interposed between the layer containing Zn, Co and Mo and the Fe-Ni diffusion layer.

Fig. 3 is a schematic explanatory view showing a method of a corrosion resistance test of the surface treated steel sheet according to the present invention for bioethanol mixed gasoline.

Fig. 4 is a schematic explanatory view showing a method of a corrosion resistance test of the surface treated steel sheet according to the present invention for bioethanol mixed gasoline.

Fig. 5 is a schematic explanatory view of a fuel supply pipe which uses the surface treated steel sheet according to the present invention, wherein (a) shows a fuel supply pipe which includes: a large-diameter pipe portion through which the fuel passes; and a small-diameter pipe portion which makes an upper portion of the large-diameter pipe portion and a lower portion of the large-diameter pipe portion communicate with each other for ventilation, and (b) shows a fuel supply pipe where a large-diameter pipe portion through which the fuel passes and a small-diameter pipe portion are formed independently.

Mode for Carrying Out the Invention

[0008]

An embodiment of the present invention is explained in detail hereinafter.

<Steel sheet>

Usually, a low carbon aluminum-killed hot-rolled coil is used as a material sheet of a surface treated steel sheet for manufacturing a pipe.

Further, a coil manufactured by using ultra low carbon steel which contains 0.003 weight% or less of carbon, or a coil manufactured by using non-aging continuous cast steel which is manufactured by further adding niobium and titanium to the ultra low carbon steel is used.

[0009]

<Pretreatment before surface treatment>

As pretreatment before surface treatment, usually, a scale (oxide film) formed on a surface of a hot-rolled steel sheet is removed by applying electrolytic cleaning or cleaning by immersion to the hot-rolled steel sheet using an alkali solution containing caustic soda as a main agent. After the scale is removed, the steel sheet is rolled in a cold-rolling step until the steel sheet obtains a product thickness (cold rolled plate).

[0010]

<Annealing>

After cleaning rolling oil which adheres to the steel sheet in rolling by electrolytic cleaning, the steel sheet is annealed. Annealing may be performed by either one of continuous annealing and box annealing, and is not limited specifically. After annealing is applied to the steel sheet, a shape of the steel sheet is modified.

[0011]

<Ni plating>

Although Ni plating is preferably applied to the steel sheet to which annealing is performed firstly, Ni plating is not inevitable.

In general, although a nickel sulfate bath which is referred to as a watt bath is mainly used as a Ni plating bath, besides the nickel sulfate bath, a sulfamic acid bath, a borofluoride bath, a chloride bath or the like can be used. A thickness of Ni plating in performing plating using these bathes is set to a value which falls within a range of 3.0μm or below. The reason of such setting of the thickness of nickel plating is described in the following column "Evaluation method".

Such plating thickness can be obtained, in a case where a typical watt bath is used, by using a bath where the bath composition contains 200 to 350g/L of nickel sulfate, 20 to 50g/L of nickel chloride and 20 to 50g/L of boric acid, pH is 3.6 to 4.6 and a bath temperature is 50 to 65°C and an electrolytic condition is set such that current density is 5 to 50A/dm^2 and the total of coulombs is approximately 900c/dm^2 or less. Although a boric acid is added as a stabilizer, a citric acid may be added in place of the boric acid.

Here, as Ni plating which is formed by a watt bath, matte Ni plating where an organic compound is not added to a plating bath except for a pit prevention agent, semi-bright Ni plating where an organic compound referred to as a leveling agent which makes a precipitated crystal surface of a plating layer smooth is added to a plating bath, and bright Ni plating where an organic compound which contains a sulfur component for making a plating layer bright by making the nickel plating crystal structure fine is added to a plating bath in addition to the leveling agent are named. Any one of these plating can be used in the present invention.

[0012]

<Formation of Fe-Ni diffusion layer>

Next, in forming a diffusion layer, heat treatment for forming a Fe-Ni diffusion layer is performed after Ni plating.

This heat treatment is provided for enhancing the adhesiveness between base steel and a plating layer by softening and recrystallizing nickel plating which is in a microcrystalline state. This heat treatment is also provided for enhancing film formability (followability) in pipe forming, bending or spool forming (rotating eccentric forming) by forming the Fe-Ni diffusion layer on the steel sheet by heat treatment.

As a method for forming the Fe-Ni diffusion layer, a method which uses a continuous annealing furnace or a method which performs diffuses Ni by heating using a box-like annealing furnace is named. A Ni diffusion temperature which falls within a range from 400°C to 800°C and a Ni diffusion time which falls within a range from 60 seconds to 12 hours are used in usual Ni diffusion by heating. However, diffusion treatment may be applied for 12 hours or more.

A diffusion gas atmosphere may be a non-oxidization protective gas atmosphere or a reduction protective gas atmosphere.

In the present invention, as a heat treatment method by box annealing, preferably used is the heat treatment which uses a protective gas consisting of 75% of hydrogen and 25% of nitrogen produced by an ammonia crack method referred to as hydrogen rich annealing with favorable heat transfer. In this method, favorable uniformity of temperature distribution is acquired in the inside of a steel strip in the longitudinal direction as well as in the widthwise direction of the steel strip and hence, the method has an advantageous effect that the irregularities in the Fe-Ni diffusion layer in the inside of the steel strip or the irregularities in the Fe-Ni diffusion layer between steel strips can be decreased.

In the diffusion treatment, when the heat treatment is continued even after iron reaches an uppermost surface of the Fe-Ni diffusion layer, a rate of iron which is exposed in an uppermost surface layer is increased.

By variously changing the heat treatment condition with respect to respective plating thicknesses, a thickness of the softened Ni layer and a thickness of the Fe-Ni diffusion layer are calculated based on a result of a glow discharge emission analysis, that is, a GDS analysis (using GDLS-5017 made by Shimazu Corporation). A large number of experiments are carried out thus preparing a large number of samples which differ in the thickness of the softened Ni layer and the thickness of the Fe-Ni diffusion layer respectively.

The GDS analysis is a measuring method by which an analysis chart in the depth direction is acquired. According to the present invention, it is regarded that Ni and Fe are respectively present until intensities of Ni and Fe become 1/10 of the maximum intensity values thereof.

The thickness of the softened Ni layer is expressed by a measured time by the GDS analysis ranging from a measured time 0 indicative of a surface layer to a measured time where intensity of Fe becomes 1/10 of the maximum intensity value.

The thickness of the Fe-Ni diffusion layer is expressed by a measured time by the GDS analysis ranging from a point of time that the intensity of Fe becomes 1/10 of the maximum intensity value to a point of time that intensity of Ni becomes 1/10 of the maximum intensity value.

With respect to the Ni plating layer before the heat treatment is performed, a thickness of the Ni plating layer is expressed by a measured time by the GDS analysis ranging from a measured time 0 indicative of a surface layer to a measured time where intensity of Ni becomes 1/10 of the maximum intensity value. The thickness of the Ni plating layer is actually measured using an X-ray fluorometric analysis.

A ratio among the measured time of the Ni plating layer by the GDS analysis, the measured time of the softened Ni plating layer by the GDS analysis and the measured time of the Fe-Ni diffusion layer by the GDS analysis is calculated, and the thickness of the softened Ni layer and the thickness of the Fe-Ni layer are calculated based on the ratio and the actual thickness of the Ni plating layer.

[0013]

<Formation of layer containing Zn, Co and Mo>

Next, a layer containing Zn, Co and Mo is formed on the

Ni plating, the Fe-Ni diffusion layer or the softened Ni layer. In a case where the Ni plating is not applied to the steel sheet in the previous step, the layer containing Zn, Co and Mo is directly formed by plating on the steel sheet to which annealing is applied.

A thickness of the layer containing Zn, Co and Mo is preferably set to a value which falls within a range of 1.0 to 8.0μm.

Such plating thickness of the layer containing Zn, Co and Mo can be obtained by using a bath where the bath composition contains180 to 280g of zinc sulfate, 10 to 70g/L of cobalt sulfate, 0.01 to 0.4g/L of ammonium molybdate, 10 to 40g/L of ammonium sulfate and 20 to 50g/L of sodium sulfate, pH is 2.7 to 3.7 and a bath temperature is 30 to 50°C, and an electrolytic condition is set such that current density is 5 to $50A/dm^2$.

A composition ratio in the plated layer containing Zn, Co and Mo is preferably set such that the content of Co is 0.1 to 5%, the content of Mo is 0.001 to 1% and a balance is formed of Zn. Such a composition ratio of the alloy plating can be realized by adjusting the above-mentioned bath composition, pH, a bath temperature, current density and the like to values which fall within preferable ranges respectively.

The schematic constitution of the steel sheet on which the layer containing Zn, Co and Mo is formed as described above is shown in Fig. 1.

Fig. 1(a) shows the constitution of the surface treated steel sheet where the layer containing Zn, Co and Mo is formed on both surfaces of the steel sheet which constitutes a substrate, and Fig. 1(b) shows the constitution of the surface treated steel sheet where Ni plating is firstly applied to both surfaces of the steel sheet which constitutes a substrate, and a layer containing Zn, Co and Mo is formed on the Ni plating.

Fig. 2(a) shows the constitution of the surface treated steel sheet where the layer containing Zn, Co and Mo and the Fe-Ni diffusion layer are formed on both surfaces of a steel sheet which constitutes a substrate with the Fe-Ni diffusion layer arranged inside the layer containing Zn, Co and Mo, and Fig. 2(b) shows the constitution of the surface treated steel sheet where a layer containing Zn, Co and Mo, a Fe-Ni diffusion layer and a softened Ni layer are formed on both surfaces of a steel sheet which constitutes a substrate with the Fe-Ni diffusion layer arranged inside the layer containing Zn, Co and Mo and with the softened Ni layer interposed between the layer containing Zn, Co and Mo and the Fe-Ni diffusion layer.

[0014]

<Evaluation method>

Evaluation specimens are prepared from steel sheets each having a layer containing Zn, Co and Mo with respective plating thicknesses and, and the corrosion resistances of the evaluation specimens are investigated by immersing these evaluation specimens into bioethanol mixed gasoline. The corrosion resistance is determined based on the presence or non-presence of generation of rust.

A corrosive liquid which experimentarily imitates bioethanol mixed gasoline is used.

The corrosive liquid is prepared as follows. 100ppm of formic acid and 200ppm of acetic acid are added to regular gasoline which is stipulated in JIS K2202, and 10% of bioethanol which is stipulated in JASO M361 is further added to the regular gasoline thus producing imitated deteriorated gasoline.

Aiming at the further enhancement of corrosiveness, corrosive water is prepared by adding 1000ppm of formic acid, 2000ppm of acetic acid and 1000ppm of chlorine to pure water, and 10weight% of the corrosive water is added to the deteriorated gasoline thus preparing a corrosive liquid.

The corrosive liquid is in a two-layered divided state where an upper layer is made of the deteriorated gasoline and a lower layer is made of the corrosive water.

An evaluation specimen is arranged in a hermetically sealed container in a state where one half of the evaluation specimen is immersed in the corrosive liquid, and the hermetically sealed container is held in a temperature controlled bath at a temperature of 45°C for a predetermined time.

As a result, as shown in Fig. 3 and Fig. 4, the evaluation specimen is formed of separated portions consisting of, in a descending order from above, a gas phase portion 11 which is brought into contact with fuel vapor (gas phase) of deteriorated gasoline, a liquid phase portion 12 which is brought into contact with deteriorated gasoline (liquid phase) and a water phase portion 13 which is brought into contact with corrosive water (water phase).

Then, the corrosion resistance of the evaluation specimen against fuel vapor is evaluated by investigating the corrosion of the gas phase portion 11 of the evaluation specimen.

With respect to the evaluation method shown in Fig. 4, the evaluation specimen which is bent at 90° with a plated surface thereof formed as an inner surface (recessed portion) is used. A radius of a valley portion is set to 1.0mm. The generation of rust in the formed valley portion is evaluated. From the result of many experiments, it is found that the generation of rust in the gas phase portion can be suppressed by setting a plating thickness of a layer containing Zn, Co and Mo to a value which falls within a range of 1.0 to 8.0μm.

Further, it is also found that by forming a Ni layer, a Fe-Ni diffusion layer or a softened Ni layer below the layer containing Zn, Co and Mo, the generation of rust in the gas phase portion can be further suppressed.

That is, from the result of experiments, it is found that when the plating thickness of the layer containing Zn, Co and Mo is less than 1.0μm, the sufficient corrosion resistance in the gas phase portion cannot be acquired.

On the other hand, when the plating thickness of the layer containing Zn, Co and Mo exceeds 8.0μm, there arises a possibility that a surface of the steel sheet is shaved in working such as pipe manufacturing thus generating abrasion powder. Accordingly, such a plating thickness is not preferable.

Further, the generation of rust in the gas phase portion can be further suppressed by forming the Ni layer, the Fe-Ni diffusion layer or the softened Ni layer below the layer containing Zn, Co and Mo. However, when the thickness of the Ni layer or the thickness of the softened Ni layer exceeds 3.0μm, a total thickness of the layer containing Zn, Co and Mo and the Ni layer or the softened Ni layer is increased so that there arises a possibility that a surface of the steel sheet is shaved in working such as pipe manufacturing thus generating abrasion powder. Accordingly, such a thickness is not preferable.

[0015]

<Pipe forming>

A pipe is manufactured using the steel sheet on which the layer containing Zn, Co and Mo (and the Ni layer, the Fe-Ni diffusion layer or the softened Ni layer) is formed. A shape of the steel sheet is modified by a leveler, and the steel sheet is slit into a predetermined outer size by a slitter. Thereafter, the steel sheet is formed into a pipe shape by a former, and longitudinal edge surfaces of the steel sheet are seam-welded to each other by high frequency induction welding thus manufacturing the pipe.

The pipe may be a fuel supply pipe for introducing fuel into a tank, a pipe for introducing fuel into an engine from a tank or a pipe for ventilation.

As shown in Fig. 5(a), a fuel supply pipe 20 is mounted on a fuel tank 23 in such a manner that the fuel supply pipe 20 extends obliquely in the upward direction from an upper portion of the fuel tank 23.

Further, a small-diameter pipe portion 22 is connected to the fuel supply pipe 20 in such a manner that a small-diameter pipe portion 22 is branched from a middle portion of a large-diameter pipe portion 21 through which fuel passes. The small-diameter pipe portion 22 makes an upper portion of the large-diameter pipe portion 21 and a lower portion of the large-diameter pipe portion 21 communicate with each other for ventilation.

The large-diameter pipe portion 21 is manufactured using the steel sheet of the present invention. The small-diameter pipe portion may be also manufactured using the steel sheet of the present invention.

The fuel supply pipe 20 defined by the present invention is not limited to a shape shown in Fig. 5(a). For example, as shown in Fig. 5(b), even when the small-diameter pipe portion 22 is mounted on the fuel tank 23 in a shape independent from the large-diameter pipe portion 21 through which fuel passes, there is no difference between the small-diameter pipe portion 22 shown in Fig. 5(b) and the small-diameter pipe portion 22 in Fig. 5(a) with respect to a point that the corrosion resistance against fuel vapor is particularly required and hence, the fuel supply pipe 20 defined by the present invention also includes the fuel supply pipe 20 shown in Fig. 5(b).

Examples

[0016]

The present invention is explained hereinafter in further detail using examples.

<Example 1>

A low carbon aluminum-killed steel sheet having a sheet thickness of 0.70mm which is manufactured through cold-rolling and annealing is used as a sheet for plating.

The composition of a steel sheet which constitutes the sheet for plating is as follows.

C: 0.045%, Mn: 0.23%, Si: 0.02%, P: 0.012%, S: 0.009%, Al: 0.063%, N: 0.0036%, balance: Fe and unavoidable impurities

The steel sheet is subjected to alkali electrolytic cleaning and pickling by immersion into a sulfuric acid and, thereafter, a layer containing Zn, Co and Mo which has a thickness of 1μm is formed on the steel sheet thus obtaining a surface treated steel sheet.

A composition ratio in the formed layer containing Zn, Co and Mo is such that the content of Co is 0.3%, the content of Mo is 0.01% and the balance is formed of Zn (% indicating mass%). The thickness and the composition ratio with respect to the layer containing Zn, Co and Mo are measured by X-ray fluorometric analysis (using ZSX 100e made by Rigaku Corporation).

[0017]

<Examples 2 to 18>

The steel sheet of the example 1 is subjected to alkali electrolytic cleaning and pickling by immersion into a sulfuric acid and, thereafter, a thickness of the layer containing Zn, Co and Mo is changed thus obtaining surface treated nickel-plated steel sheets of the examples 2 to 18 shown in Table 1.

With respect to the examples 2 to 18 where Ni plating is applied to the steel sheet, a numerical value of a thickness of the Ni plating is described. With respect to the examples 2 to 18 where Ni plating is not applied to the steel sheet, 0 is described as a thickness of the Ni plating.

With respect to Ni plating, a plating thickness is changed under conditions where matte plating and a watt bath are adopted.

Other conditions are set equal to the corresponding conditions used in the example 1. The thickness of Ni plating is measured by X-ray fluorometric analysis (using ZSX 100e made by Rigaku Corporation).

[0018]

<Example 19>

The steel sheet of the example 1 is subjected to alkali electrolytic cleaning and pickling by immersion into a sulfuric acid and, thereafter, nickel plating having a plating thickness of 2μm is applied to the steel sheet under conditions where matte plating and a watt bath are adopted thus obtaining a nickel-plated steel sheet. Thereafter, heat diffusion treatment is applied to the nickel-plated steel sheet under conditions where 800°C and 1min are adopted thus forming a Fe-Ni diffusion layer having a thickness of 1.23μm on a surface of the steel sheet.

Thereafter, a layer containing Zn, Co and Mo which has a thickness of 1μm is formed on the Fe-Ni diffusion layer by plating thus obtaining a surface treated steel sheet of the example 19 shown in Table 2.

The composition ratio of the formed plated layer containing Zn, Co and Mo is equal to the composition ratio of the formed plated layer of the example 1.

[0019]

<Examples 20 to 32>

Steel sheets of the examples 20 to 32 shown in Table 2 are obtained by changing a thickness of the layer containing Zn, Co and Mo.

In the examples 20 to 32, with respect to the examples where a softened Ni layer is formed between the layer containing Zn, Co and Mo and the Fe-Ni diffusion layer, a numerical value of a thickness of the softened Ni layer is described. With respect to examples where a softened Ni layer is not formed between the layer containing Zn, Co and Mo and the Fe-Ni diffusion layer, 0 is described as a thickness of the softened Ni layer.

In Ni plating, a plating thickness is changed under conditions where matte plating and a watt bath are adopted. The thickness of Ni plating is measured by X-ray fluorometric analysis (using ZSX 100e made by Rigaku Corporation). Other conditions except for the thickness of the layer containing Zn, Co and Mo, the thickness of Ni plating and the heat diffusion treatment described in Table 2 are set equal to the corresponding conditions used in the example 19.

[0020]

<Comparison example>

Surface treated steel sheets of the comparison examples 1 to 5 shown in Table 1 are obtained by changing a thickness of the layer containing Zn, Co and Mo and a thickness of the Ni layer.

Further, the thickness of the layer containing Zn, Co and Mo, the thickness of Ni plating and the heat diffusion treatment are changed as described in Table 2, and other conditions except for the thickness of the layer containing Zn, Co and Mo, the thickness of Ni plating and the heat diffusion treatment are set equal to the corresponding conditions of the example 19 thus obtaining surface treated steel sheets of the comparison examples 6 to 11 shown in Table 2.

[0021]

<Evaluation>

Next, evaluation specimens are prepared from the respective plated steel sheets of the examples and the comparison examples. After holding the evaluation specimens in the temperature-controlled bath at a temperature of 45°C for 500 hours, the appearance of a gas phase portion of each evaluation specimen is observed for investigating the generation of rust. The result of the investigation is shown in a column "result of rust generation in gas phase portion" in Table 1 and Table 2.

[0022]

[Table 1]

	thickness of layer containing Zn, Co and Mo (μm)	Thickness of nickel plating (μm)	result of rust generation in gas phase portion
example 1	1	0	not observed
example 2	1	1	not observed
example 3	1	2	not observed
example 4	1	3	not observed
example 5	2	0	not observed
example 6	3	0	not observed
example 7	3	1	not observed

example 8	3	2	not observed
example 9	5	0	not observed
example 10	5	1	not observed
example 11	5	2	not observed
example 12	7	0	not observed
example 13	7	1	not observed
example 14	7	2	not observed
example 15	8	0	not observed
example 16	8	1	not observed
example 17	8	2	not observed
example 18	8	3	not observed
comparison example 1	0.5	0	observed
comparison example 2	0.75	0	observed
Comparison example 3	0.75	1	observed
comparison example 4	0.75	2	observed
comparison example 5	0.9	0	observed

[0023]

[Table 2]

	thickness of layer containing Zn, Co and Mo (μm))	softened Ni layer (μm)	Fe-Ni diffusion layer (μm)	result of rust generation in gas phase portion
example 19	1	0	1.23	not observed
example 20	1	0	2.34	not observed
example 21	1	0.9	1.47	not observed
example 22	1	0.82	3.34	not observed
example 23	1	1.24	2.78	not observed
example 24	1	2.97	2.24	not observed
example 25	2	0	2.34	not observed
example 26	2	2.97	2.24	not observed
example 27	5	0	2.34	not observed
example 28	5	2.97	2.24	not observed
example 29	7	0	2.34	not observed
example 30	7	2.97	2.24	not observed
example 31	8	0	2.34	not observed
example 32	8	2.97	2.24	not observed
comparison example 6	0.5	0	1.23	observed

comparison example 7	0.5	0	2.34	observed
comparison example 8	0.5	0.9	1.47	observed
comparison example 9	0.5	0.82	3.34	observed
comparison example 10	0.75	1.24	2.78	observed
comparison example 11	0.75	2.97	2.24	observed

[0024]

As can be clearly understood from Table 1 and Table 2, the generation of rust is not observed with respect to the surface treated steel sheets of the examples 1 to 32 of the present invention and hence, these steel sheets are excellent as a raw material for manufacturing pipes having corrosion resistance against fuel vapor.

The above-mentioned corrosive liquid generates vapor having stronger corrosiveness than gasoline, light oil, bioethanol or bio-diesel fuel and hence, it is considered that no generation of rust in the test using such a corrosive liquid means no generation of rust also against gasoline, light oil, bioethanol or bio-diesel fuel.

On the other hand, rust is generated in the surface treated steel sheets of the comparison examples 1 to 11 and hence, these steel sheets have poor practicability as a raw material for manufacturing a pipe having corrosion resistance against fuel vapor.

Industrial applicability

[0025]

The surface treated steel sheet for manufacturing a pipe according to the present invention can suppress the generation of rust when the steel sheet is exposed to fuel vapor of fuel such as gasoline, light oil, bioethanol or bio-diesel fuel.

Further, the pipe and the fuel supply pipe manufactured using the surface treated steel sheet for manufacturing a fuel supply pipe according to the present invention has excellent corrosion resistance against fuel vapor and hence, these pipes have extremely high industrial applicability.

Description of Reference Numbers and Signs

[0026]

11: gas phase portion

12: liquid phase portion

13: water phase portion

20: fuel supply pipe

21: large-diameter pipe portion

22: small-diameter pipe portion

23: fuel tank