

**(12) STANDARD PATENT**  
**(19) AUSTRALIAN PATENT OFFICE**

(11) Application No. **AU 2018210488 B2**

(54) Title  
**Method and device for manufacturing black plated steel sheet**

(51) International Patent Classification(s)  
**C23C 8/16** (2006.01) **C23C 2/26** (2006.01)  
**C23C 2/06** (2006.01) **C23C 28/00** (2006.01)

(21) Application No: **2018210488** (22) Date of Filing: **2018.01.17**

(87) WIPO No: **WO18/135518**

(30) Priority Data

(31)	Number	(32)	Date	(33)	Country
	<b>2017-006606</b>		<b>2017.01.18</b>		<b>JP</b>

(43) Publication Date: **2018.07.26**

(44) Accepted Journal Date: **2022.12.22**

(71) Applicant(s)  
**Nippon Steel Nisshin Co., Ltd.**

(72) Inventor(s)  
**Yamamoto, Masaki; Nakano, Tadashi; Takahashi, Ichiro; Nakamizo, Hiroyuki; Sato, Toshiaki; Kurisu, Yoshinobu; Sakuraba, Yuuki; Yukura, Yoshitaka; Ohta, Tsutomu; Kajimoto, Shinichi; Suzuki, Noboru; Tsuchiyama, Masahiko; Murai, Yuusuke**

(74) Agent / Attorney  
**Halfords IP, GPO Box 4212, Sydney, NSW, 2001, AU**

(56) Related Art  
**US 2015/0083276 A1**  
**EP 3425081 A1**

(12) 特許協力条約に基づいて公開された国際出願

(19) 世界知的所有権機関  
国際事務局

(43) 国際公開日  
2018年7月26日(26.07.2018)



(10) 国際公開番号

WO 2018/135518 A1

(51) 国際特許分類:

C23C 8/16 (2006.01)

C23C 2/26 (2006.01)

C23C 2/06 (2006.01)

C23C 28/00 (2006.01)

(21) 国際出願番号: PCT/JP2018/001153

(22) 国際出願日: 2018年1月17日(17.01.2018)

(25) 国際出願の言語: 日本語

(26) 国際公開の言語: 日本語

(30) 優先権データ:

特願 2017-006606 2017年1月18日(18.01.2017) JP

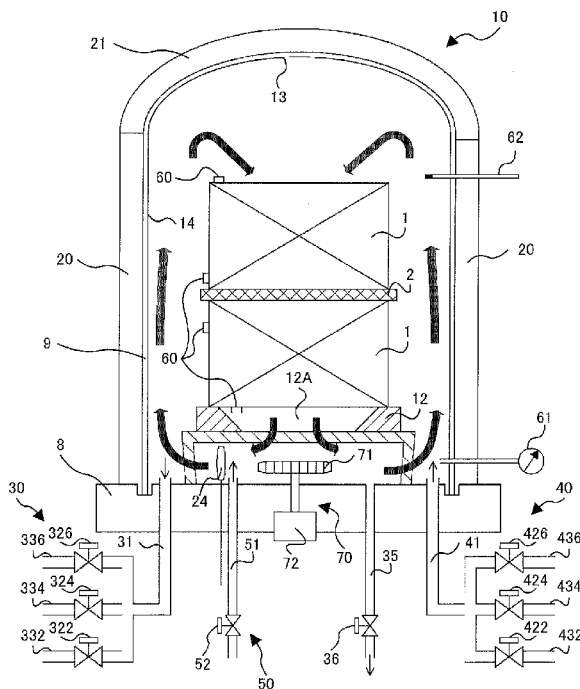
(71) 出願人: 日新製鋼株式会社(NISSHIN STEEL CO., LTD.) [JP/JP]; 〒1008366 東京都千代田区丸の内三丁目4番1号 Tokyo (JP).

(72) 発明者: 山本 正樹 (Yamamoto Masaki); 〒1008366 東京都千代田区丸の内三丁目4番1号 日新製鋼株式会社内 Tokyo (JP). 中野忠 (NAKANO Tadashi); 〒1008366 東京都千代田区丸の内三丁目4番1号 日新製鋼株式会社内 Tokyo (JP). ▲高▼橋 一郎(TAKAHASHI

Ichiro); 〒1008366 東京都千代田区丸の内三丁目4番1号 日新製鋼株式会社内 Tokyo (JP). 中溝 浩行(NAKAMIZO Hiroyuki); 〒1008366 東京都千代田区丸の内三丁目4番1号 日新製鋼株式会社内 Tokyo (JP). 佐藤 敏明(SATO Toshiaki); 〒1008366 東京都千代田区丸の内三丁目4番1号 日新製鋼株式会社内 Tokyo (JP). 栗栖 義信(KURISU Yoshinobu); 〒1008366 東京都千代田区丸の内三丁目4番1号 日新製鋼株式会社内 Tokyo (JP). 櫻庭 雄樹(SAKURABA Yuuki); 〒1008366 東京都千代田区丸の内三丁目4番1号 日新製鋼株式会社内 Tokyo (JP). 湯倉 義孝(YUKURA Yoshitaka); 〒7370051 広島県呉市中央一丁目2番3号 日新工機株式会社内 Hiroshima (JP). 太田 勉(OHTA Tsutomu); 〒7370051 広島県呉市中央一丁目2番3号 日新工機株式会社内 Hiroshima (JP). 梶本 真一(KAJIMOTO Shinichi); 〒7370051 広島県呉市中央一丁目2番3号 日新工機株式会社内 Hiroshima (JP). 鈴木 昇(SUZUKI Noboru); 〒8068586 福岡県北九

(54) Title: METHOD AND DEVICE FOR MANUFACTURING BLACK PLATED STEEL SHEET

(54) 発明の名称: 黒色めっき鋼板の製造方法およびその製造装置



(57) Abstract: The present invention relates to a method for manufacturing a black plated steel sheet by bringing a molten Al- and Mg-containing Zn-plated steel sheet into contact with water vapor in a sealed container, and provides a method for manufacturing a black plated steel sheet whereby a plating layer is uniformly blackened and improve appearance is obtained. A method for manufacturing a black plated steel sheet by bringing a molten Al- and Mg-containing Zn-plated steel sheet 1 into contact with water vapor in a sealed container 10, the sealed container 10 being configured so that either the flow rate of water vapor introduced into the sealed container 10 or the flow rate of water vapor discharged from the sealed container 10 is variably controlled, whereby the pressure in the sealed container 10 is maintained at a predetermined value, and the water vapor introduced into the sealed container 10 and the molten Al- and Mg-containing Zn-plated steel sheet 1 being brought into contact with each other in the sealed container 10 in which the pressure thereof can be maintained at the predetermined value.



州市八幡西区東浜町 1 番 1 号 黒崎播磨株式会社内 Fukuoka (JP). 土山 雅彦(TSUCHIYAMA Masahiko); 〒8068586 福岡県北九州市八幡西区東浜町 1 番 1 号 黒崎播磨株式会社内 Fukuoka (JP). 村井 裕輔(MURAI Yuusuke); 〒8068586 福岡県北九州市八幡西区東浜町 1 番 1 号 黒崎播磨株式会社内 Fukuoka (JP).

(74) 代理人: 納谷 洋弘, 外(NAYA Hiromitsu et al.); 〒5410041 大阪府大阪府中央区北浜四丁目 7 番 2 8 号 住友ビルディング第 2 号館 7 階 Osaka (JP).

(81) 指定国(表示のない限り、全ての種類の国内保護が可能): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JO, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) 指定国(表示のない限り、全ての種類の広域保護が可能): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), ユーラシア (AM, AZ, BY, KG, KZ, RU, TJ, TM), ヨーロッパ (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

添付公開書類:

一 国際調査報告 (条約第21条(3))

(57) 要約: 溶融 Al、Mg 含有 Zn めっき鋼板を密閉容器中で水蒸気と接触させて黒色めっき鋼板の製造方法に関し、めっき層を均一に黒色化してより見栄えの良い黒色めっき鋼板を製造する方法を提供する。溶融 Al、Mg 含有 Zn めっき鋼板 1 を密閉容器 10 中で水蒸気と接触させて黒色めっき鋼板を製造する方法であって、前記密閉容器 10 は、当該密閉容器 10 内に導入される水蒸気の流量と当該密閉容器 10 内から排出される水蒸気の流量とのうち少なくともいずれか一方が可変制御されることにより、当該密閉容器 10 内の圧力が所定値に維持されるように構成されており、圧力が前記所定値に維持されうる前記密閉容器 10 内において、当該密閉容器 10 内に導入された水蒸気と、前記溶融 Al、Mg 含有 Zn めっき鋼板 1 とを接触させる。

# METHOD AND DEVICE FOR MANUFACTURING BLACK PLATED STEEL SHEET

## BACKGROUND OF THE INVENTION

### FIELD OF THE INVENTION

[0001] The present invention relates to a method and a device for manufacturing a black coated steel sheet.

### DESCRIPTION OF THE BACKGROUND ART

[0002] Needs for steel sheets of black appearance have been growing, with a design awareness, in the field of roofing and exterior materials for buildings, home appliances, automobiles, and the like. As a surface blackening method for steel sheets, there has been adopted a method of applying black paint to a surface so as to form a black paint film thereon, and there has been proposed a method of blackening, without forming any black paint film, a plating layer (coating layer) itself by oxidation so as to shield a metallic gloss and silver-white tone of a substrate portion of plated steel sheets (coated steel sheets). A method is described, in e.g. Patent Document 1, by which steam has been brought into contact with hot-dip zinc-aluminum-magnesium (Zn-Al-Mg) alloy coated steel sheets in a sealed chamber, thereby forming a blackened oxide film in the hot-dip Zn-Al-Mg alloy coating layer.

[0003] Another method is described, in Patent Document 2, by which steam has been brought into contact with plated steel sheets (coated steel sheets) while spacers being interposed among the plated steel sheets, thereby enabling steam to have contact with the plated steel sheets in the same manner between their central portions and peripheral portions, which results in more uniform blackening of a surface of the plating layer (coating layer).

[0004] Hereinafter, in the present specification, hot-dip Zn-Al-Mg alloy coated steel sheets will be occasionally referred to as "coated steel sheets" for short. Further, a hot-dip Zn-Al-Mg alloy coating layer of the hot-dip Zn-Al-Mg alloy coated steel sheets will be occasionally referred to as "coating layer" for short. Still further, a contact treatment by which steam is brought into contact with hot-dip Zn-Al-Mg alloy coated steel sheets in a sealed chamber so as to blacken the hot-dip Zn-Al-Mg alloy coating layer will be occasionally referred to as "steam treatment" for short.

[0005] (Prior Art Document)  
(Patent Document)

Patent Document 1: Japanese Patent No. 5335159

Patent Document 2: Japanese Patent Application Publication No. 2013-241676

[0006] (Problem to be solved)

As described above, for more uniform blackening of the coating layer, it is quite essential that steam be distributed sufficiently around a whole area of the coated steel sheets to be blackened so as to have uniform contact with a surface of the coating layer.

[0007] However, when manufacturing the black coated steel sheets through the steam

treatment in the above-described conventional method, there has been arisen a problem that the manufactured black coated steel sheets sometimes do not have uniformly black appearance. A probable cause of such a non-uniform problem is considered, as a result of various examinations, to be that a necessary amount of steam for the steam treatment is not distributed around the coated steel sheets to be blackened in the sealable chamber.

### SUMMARY OF THE INVENTION

[0008] In view of the above-described problems, the present invention seeks to provide a method for manufacturing a black coated steel sheet having further enhanced appearance as a result of uniformly blackening a coating layer.

[0009] (Means for Solving Problems)

[1] The present invention provides a method for manufacturing a black coated steel sheet by bringing steam into contact with a hot-dip Zn-Al-Mg alloy coated steel sheet under a closed atmosphere, the method comprising a step of, in a sealable chamber configured such that pressure therein is maintained at a predetermined value through variable control of an amount of steam flowing into the sealable chamber and/or an amount of steam flowing out of the sealable chamber, allowing contact to occur between: the hot-dip Zn-Al-Mg alloy coated steel sheet; and the steam introduced into the sealable chamber whose internal pressure could be maintained at the predetermined value.

[0010] [2] In the method for manufacturing the black coated steel sheet of the above [1], the predetermined value is higher than or equal to 80% as well as lower than or equal to 120% of a value predetermined for pressure in the sealable chamber.

[0011] [3] The present invention provides a device for manufacturing a black coated steel sheet by bringing steam into contact with a hot-dip Zn-Al-Mg alloy coated steel sheet under a closed atmosphere, the device comprising: a sealable chamber configured to allow the hot-dip Zn-Al-Mg alloy coated steel sheet to be arranged therein; and a pressure control unit configured to variably control an amount of steam flowing into the sealable chamber and/or an amount of steam flowing out of the sealable chamber, so as to maintain pressure in the sealable chamber at a predetermined value, wherein, in the sealable chamber whose internal pressure could be maintained at the predetermined value, by the pressure control unit, the hot-dip Zn-Al-Mg alloy coated steel sheet and the steam introduced into the sealable chamber are allowed to have contact with each other.

[0012] [4] In the device for manufacturing a black coated steel sheet of the above [3], the predetermined value is higher than or equal to 80% as well as lower than or equal to 120% of a value predetermined for pressure in the sealable chamber.

[0013] According to the above-configured [1] or [3],

when steam is brought into contact with the hot-dip Zn-Al-Mg alloy coated steel sheet in the sealable chamber for blackening,

by causing steam to flow into the sealable chamber through an inlet, and causing steam to flow out of the sealable chamber through an outlet,

hydrogen gas generated as a result of a blackening reaction with steam could be discharged appropriately from the sealable chamber, while a necessary amount of steam could be secured in the sealable chamber.

The sealable chamber is configured such that an internal pressure therein could be maintained at a predetermined value through variable control of an amount of steam flowing into the sealable chamber and/or an amount of steam flowing out of the sealable chamber.

[0014] According to the above-configured [2] or [4],  
depending upon the circumstances of the steam treatment for the coated steel sheet in the sealable chamber,  
the internal pressure is appropriately controlled within a range of 80% to 120% with respect to a value predetermined for pressure in the sealable chamber during the steam treatment, thereby enabling the manufacture of a high-quality black coated steel sheet.

[0014a] According to one aspect, the present invention provides a method for manufacturing a black coated steel sheet by bringing steam into contact with a hot-dip Zn-Al-Mg alloy coated steel sheet under a closed atmosphere, the method comprising a step of, in a sealable chamber configured such that an amount of steam flowing into the sealable chamber and an amount of atmospheric gas flowing out of the sealable chamber are variably controllable, maintaining an internal pressure in the sealable chamber, while causing steam to flow into the sealable chamber through the use of a plurality of pipes, and causing atmospheric gas to flow out of the sealable chamber through the use of a plurality of pipes, in parallel with each other, so as to prohibit hydrogen gas generated in the sealable chamber from remaining therein, thereby to allow contact to occur between: the hot-dip Zn-Al-Mg alloy coated steel sheet; and the steam introduced into the sealable chamber.

[0014b] According to a further aspect, the present invention provides a method for manufacturing a black coated steel sheet by bringing steam into contact with a hot-dip Zn-Al-Mg alloy coated steel sheet under a closed atmosphere, the method comprising a step of, in a sealable chamber configured such that at least one of an amount of steam flowing into the sealable chamber and an amount of atmospheric gas flowing out of the sealable chamber are variably controllable, maintaining an internal pressure in the sealable chamber at between 80% and 120% of a predetermined value, while causing steam to flow into the sealable chamber through the use of a plurality of pipes, and causing atmospheric gas to flow out of the sealable chamber through the use of a plurality of pipes, in parallel with each other, through variable control of at least one of an amount of the steam flowing into the sealable chamber and an amount of the atmospheric gas flowing out of the sealable chamber, so as to prohibit hydrogen gas generated in the sealable chamber from remaining therein, thereby to allow contact to occur between: the hot-dip Zn-Al-Mg alloy coated steel sheet; and the steam introduced into the sealable chamber.

[0014c] According to a further aspect, the present invention provides a device for manufacturing a black coated steel sheet by performing treatment of bringing steam into contact with a hot-dip Zn-Al-Mg alloy coated steel sheet under a closed atmosphere, the device comprising: a sealable chamber configured to allow the hot-dip Zn-Al-Mg alloy coated steel sheet to be arranged therein; a plurality of introduction pipes for steam to flow into the sealable chamber; a plurality of discharge pipes for atmospheric gas to flow

out of the sealable chamber; and a pressure control unit configured to variably control an amount of steam flowing into the sealable chamber through the plurality of introduction pipes, and to variably control an amount of atmospheric gas flowing out of the sealable chamber through the plurality of discharge pipes, so as to maintain an internal pressure in the sealable chamber at a predetermined value, wherein, the pressure control unit is further configured to, during treatment of bringing the steam into contact with the hot-dip Zn-Al-Mg alloy coated steel sheet, maintain the internal pressure in the sealable chamber, while cause the steam to flow into the sealable chamber, and cause the atmospheric gas to flow out of the sealable chamber, in parallel with each other, so as to prohibit hydrogen gas generated in the sealable chamber from remaining therein.

[0014d] According to a further aspect, the present invention provides a device for manufacturing a black coated steel sheet by performing treatment of bringing steam into contact with a hot-dip Zn-Al-Mg alloy coated steel sheet under a closed atmosphere, the device comprising a sealable chamber configured to allow the hot-dip Zn-Al-Mg alloy coated steel sheet to be arranged therein; a plurality of introduction pipes for steam to flow into the sealable chamber; a plurality of discharge pipes for atmospheric gas to flow out of the sealable chamber; and a pressure control unit configured to variably control at least one of an amount of steam flowing into the sealable chamber through the plurality of introduction pipes, and an amount of atmospheric gas flowing out of the sealable chamber through the plurality of discharge pipes, so as to maintain an internal pressure in the sealable chamber at a predetermined value, wherein the pressure control unit is further configured to, during treatment of bringing the steam into contact with the hot-dip Zn-Al-Mg alloy coated steel sheet, maintain the internal pressure in the sealable chamber at between 80% and 120% of a predetermined value, while cause the steam to flow into the sealable chamber, and cause the atmospheric gas to flow out of the sealable chamber, in parallel with each other, through variable control of at least one of an amount of the steam flowing into the sealable chamber and an amount of the atmospheric gas flowing out of the sealable chamber, so as to prohibit hydrogen gas generated in the sealable chamber from remaining therein.

[0015] (Advantageous Effects of the Invention)

According to the present invention, there could be provided a method for manufacturing a high-quality black coated steel sheet of enhanced appearance.

### BRIEF DESCRIPTIONS OF THE DRAWINGS

[0016] For more thorough understanding of the present invention and advantages thereof, the following descriptions should be read in conjunction with the accompanying drawings in which:

FIG. 1 depicts a flow chart of a method for manufacturing black coated steel sheets according to the present invention.

FIG. 2 depicts a schematic view of a device for manufacturing black coated steel sheets according to the present invention.

FIG. 3 depicts a block diagram indicating a control system of a device for manufacturing black coated steel sheets according to the present invention.

### DESCRIPTIONS OF EMBODIMENTS OF THE INVENTION

[0017] [Method for Manufacturing Black Coated Steel Sheets]

The method for manufacturing black coated steel sheets according to the present invention includes a method of bringing steam into contact with hot-dip Zn-Al-Mg alloy coated steel sheets in a sealable chamber so as to manufacture black coated steel sheets.

[0018] As shown in the flow chart of FIG. 1, the method according to the present invention is performed in the following order of five steps:

first step (S110) of heating hot-dip Zn-Al-Mg alloy coated steel sheets arranged in a sealable chamber;

second step (S120) of discharging atmospheric gas from the sealable chamber so as to reduce a gas pressure in the sealable chamber to 70 kPa or lower;

third step (S130) of introducing steam into the sealable chamber and blackening a coating layer of coated steel sheets at a predetermined pressure;

fourth step (S140) of, after the third step (S130), returning an internal pressure of the sealable chamber to a value of the outside air pressure, and thereafter, reducing a gas pressure in the sealable chamber to 70 kPa or lower again; and

fifth step (S150) of cooling the coated steel sheets in the sealable chamber.

It is to be noted that “atmospheric gas” means gases present in the sealable chamber, and more specifically, such an atmospheric gas is a generic term indicative of the outside air, steam, hydrogen-containing steam, nitrogen gas, and so forth.

[0019] Hereinafter, a detailed explanation will be provided for each step.

[0020] (First Step)

In the first step (S110), the coated steel sheets arranged are heated in the sealable chamber.

[0021] The sealable chamber (10) includes an arrangement portion (12) for arranging therein the coated steel sheets (1), and has strength sufficient at least for withstanding the pressure reduction caused by discharging atmospheric gas therefrom, the steam introduction thereinto, the heat application thereto, the cooling thereof, and the like. The sealable chamber (10) is configured such that it is capable of being in a closed state to substantially prevent gas from flowing thereinto from outside or in an open state to allow coated steel sheets to be brought therein from outside. The sealable chamber (10) has openings for connecting with pipes such as a gas discharge pipe (31), steam supply pipe (41), gas introduction pipe (51), drain pipe (35), which will be described later, formed at wall or bottom surfaces thereof, and the sealable chamber (10) is further configured such that it is rendered in a closed state by closing valves provided on the pipes. Furthermore, the sealable chamber (10) may be provided, on an exterior wall surface thereof, with temperature regulation mechanisms (20, 21) for the heat application thereto or the cooling thereof so as to regulate the temperature therein.

[0022] Each of the coated steel sheets (1) has a substrate steel sheet, and a hot-dip Zn-Al-Mg alloy coating layer formed on a surface of the substrate steel sheet.

[0023] The substrate steel sheet is not particularly restricted on its type, and e.g., low carbon steel, medium carbon steel, high carbon steel, or alloy steel may be adopted for



such a substrate steel sheet. If a good press formability is required, it is preferable that a deep drawing steel sheet, such as Ti or Nb-containing low-carbon steel sheets, be adopted for the substrate steel sheet. Furthermore, a high-strength steel sheet containing P, Si, Mn, or the like may also be adopted.

[0024] The hot-dip Zn-Al-Mg alloy coating layer is so configured at least in composition as to provoke blackening by bringing steam into contact with this coating layer. A blackening mechanism for the coating layer in contact with steam has been unclarified. It is speculated, as one hypothesis, that oxides (such as  $\text{ZnO}_{1-x}$ ) and hydroxides of Zn, Al, and Mg having an oxygen-deficient type defective structure would be generated on a surface and in a bulk of the coating layer, upon being in contact with steam. When the oxygen-deficient type oxides and hydroxides are generated in such a manner, light is trapped in defects of energy levels, provoked by those oxides and hydroxides, and as a result, such oxides and hydroxides exhibit black appearance. The Zn-Al-Mg alloy coating layer, e.g., generated at a ratio of: 0.1 to 60 wt% of Al; 0.01 to 10 wt% of Mg; and the rest of Zn could be preferably blackened, by bringing steam into contact with this coating layer.

[0025] The most distributed hot-dip Zn-Al-Mg alloy coated steel sheets in the market are those having coating layers containing approximately 6 wt% of Al and approximately 3 wt% of Mg. The metal texture of such a coating layer is an Al-Zn- $\text{Zn}_2\text{Mg}$  ternary eutectic texture having: primary Al phase; or primary Al phase and Zn single phase mixed, in a base of this ternary eutectic texture, and the coating layer could be preferably blackened through the steam treatment. The phases (Al phase, Zn phase, and  $\text{Zn}_2\text{Mg}$  phase) have individually irregular sizes and forms, and are mutually intermingled. The primary Al phase and the Al phase in the Al-Zn- $\text{Zn}_2\text{Mg}$  ternary eutectic texture originate from the Al' phase at high temperature in the Al-Zn-Mg ternary equilibrium diagram (which Al' phase is a phase of Al solid solution having Zn dissolving therein and containing a small amount of Mg). At ordinary temperatures, the Al' phase emerging at high temperature usually emerges as separated phases of fine Al phase and fine Zn phase. The Zn phase in the ternary eutectic texture is a phase of Zn solid solution having a small amount of Al dissolving therein, and possibly, further having Mg dissolving therein. The  $\text{Zn}_2\text{Mg}$  phase in the ternary eutectic texture is intermetallic compound phase present in the vicinity of a point with respect to approximately 84 wt% of Zn in the Zn-Mg binary equilibrium diagram.

[0026] The coating layer capable of being preferably blackened by bringing steam into contact with this coating layer is not limited only to a coating layer whose metal texture is the Al-Zn- $\text{Zn}_2\text{Mg}$  ternary eutectic texture having: primary Al phase; or primary Al phase and Zn single phase mixed, in a base of this ternary eutectic texture. The coating layer may also be a coating layer whose metal texture has Zn phase or intermetallic compound phase as primary phase, where an intermetallic compound originates from other elements, such as Si, contained in this coating layer. Furthermore, the Al-Zn- $\text{Zn}_2\text{Mg}$  ternary eutectic texture may be replaced by intermetallic compounds such as  $\text{Zn}_2\text{Mg}$  and  $\text{Zn}_{11}\text{Mg}_2$ . Upon being in contact with steam, these intermetallic compounds also generate oxides and hydroxides of Zn, Al, and Mg having an oxygen-deficient type defective structure on a surface and in a bulk of the coating layer, and their provoked defects of energy levels trap light therein, and as a result, such oxides and hydroxides exhibit black appearance.

[0027] There are no particular restrictions on the thickness of the coating layer. The thickness is preferably 3 to 100  $\mu\text{m}$ . If the thickness of the coating layer is 3  $\mu\text{m}$  or greater, the handling of the coated steel sheets (1) is less likely to allow scars to reach the substrate steel sheet. As a result, the coated steel sheets (1) are improved in black-appearance retention as well as corrosion resistance. At the same time, if the thickness of the coating layer is 100  $\mu\text{m}$  or smaller, the coating layer and the substrate steel sheet are less likely to be separated from each other, in a process unit, where such separation occurs due to differences in ductility between the coating layer and the substrate steel sheet, upon being compressed.

[0028] There are no particular restrictions on the form of the coated steel sheets (1) insofar as the coating layer of an area to be blackened could have contact with steam. The coated steel sheets (1) could be coated with, e.g., a flat coating layer (such as plate form) or a curved coating layer (such as coil form). The "coil form" means that the coated steel sheets (1) are recoverably deformed such that they are rolled with intervals in a radial direction. The coated steel sheets (1) are preferably in coil form, from the viewpoint of the ease with which such steel sheets could be arranged inside the sealable chamber (10) and could be carried before and after the process. If the coated steel sheets (1) are in coil form, each interval in the radial direction, the shortest distance between adjacent surfaces in particular, is preferably 0.05 mm or longer to facilitate the infiltration of steam.

[0029] Further, spacers are allowed to be interposed between surfaces of the coated steel sheets (1) rolled into coil form to maintain the above-described intervals. The spacers have a form at least such that steam could be distributed sufficiently around a surface of the coating layers of the coated steel sheets (1) in coil form, and from this regard, the spacers may be in either linear or planar shape. Linear spacers are arranged, in part, on a surface of the coated steel sheets (1), and planar spacers are arranged, at least in part, on the surface of the coated steel sheets (1). The contact area between the spacers and the surface of the coated steel sheets (1) is preferably small, and more specifically, as small as 15  $\text{mm}^2$  or smaller, at each contact point. There are no particular restrictions on material of the spacers unless such material significantly deteriorates and ignites, or fuses with the coated steel sheets or dissolves in the coated steel sheets during the steam treatment. The material of the spacers is preferably metal or resin, and more preferably, permeable to steam.

[0030] Still further, if an unblackened part of the surface of the coated steel sheets (1) is to be left by design, such an unblackened part may be created by masking with aluminum tape or resin tape.

[0031] Still further, when arranging the coated steel sheets (1) in the sealable chamber (10), such arrangement may be made in the form of a single layer or a stack of a plurality of layers. In the form of single layer, each of the above-described coated steel sheets (1) in coil form, e.g., may be arranged in an eye-to-sky position. In the form of stack of a plurality of layers, if two or more of the above-described coated steel sheets (1) in coil form, e.g., are to be blackened at the same time, they may be so arranged as to be stacked in an eye-to-sky position in the sealable chamber (10). When arranging the coated steel sheets (1) in the sealable chamber (10), adjacent layers of coated steel sheets preferably

have the above-described interval of 0.05 mm or longer, e.g., by interposing a spacer therebetween to facilitate the infiltration of steam. Furthermore, the coated steel sheets (1) to be blackened in the sealable chamber (10) may have any arbitrarily formed shape. The coated steel sheets (1) in such an arbitrarily formed shape may be placed on or suspended from a shelf installed in the sealable chamber (10).

[0032] Still further, in the first step (S110), the coated steel sheets (1) are heated in the presence of gas (low-steam gas) whose dew point is lower than the temperature of the coated steel sheets (1) at all times. In other words, the atmospheric gas present in the sealable chamber (10) is to be low-steam gas. For the low-steam gas, the outside air may be adopted from the viewpoint of the facility with which the coated steel sheets (1) could be heated. The outside air may be replaced, however, by the inert gas such as nitrogen, insofar as the coated steel sheets (1) could be blackened, or the outside air may be replaced by some atmosphere lower in dew point than the outside air. The low-steam gas could be introduced into the sealable chamber (10) through a gas introduction unit (50) connected to the sealable chamber (10). In the present specification, gas whose dew point is lower than the temperature of the coated steel sheets (1) will be referred to as "low-steam gas."

[0033] Usually, the temperature of the coated steel sheets (1) is at an ordinary level before heating, and the coated steel sheets (1) have a large heat capacity. Under such circumstances, if the coated steel sheets (1) are heated in the presence of steam-enriched atmospheric gas whose dew point can be higher than the temperature of the coated steel sheets (1), there are probabilities that the atmospheric gas would be cooled in the vicinity of the surface of the coated steel sheets (1). As a result, the coated steel sheets (1) are subjected to the dew condensation of the atmospheric gas on their surface. Further, a part, on which the dew condensation occurs, of the coated steel sheets (1) is prohibited from the steam-contact and blackening, and for this reason, there are probabilities that the coating layer would be hindered from being uniformly blackened. Still further, there are probabilities that the condensed dew would erode the surface of the coated steel sheets (1), followed by the white-rust formation spoiling their appearance.

[0034] Against such a matter, in the first step (S110) as an embodiment according to the present invention, the coated steel sheets (1) are heated in the presence of the low-steam gas. This restrains the dew formation, and therefore, enables more uniform blackening of the coating layer and further enhanced appearance of the coated steel sheets (1). It is further preferred, therefore, that the dew point of the atmospheric gas in the first step (S110) be lower than or equal to an ordinary temperature. For the atmospheric gas in this step, the outside air, e.g., may be adopted. As the temperature of the coated steel sheets (1) increases with increase in heating, the dew point of the atmospheric gas is at all times lower than the temperature of the coated steel sheets (1) on the assumption that such a dew point would be lower than the temperature of the coated steel sheets (1) at a start of heating, thereby preventing the dew formation on the coated steel sheets (1).

[0035] In the first step (S110), the coated steel sheets (1) are heated until the surface temperature of the coating layer reaches a level at which the coating layer is blackened as a result of being in contact with steam (which will be, hereinafter, occasionally referred to as "blackening temperature"). The coated steel sheets (1) arranged in the sealable

chamber (10) may be heated to above the blackening temperature while the surface temperature being measured, e.g., through a temperature sensor.

[0036] It is to be noted that, due to a large heat capacity of the coated steel sheets (1), there are some probabilities that the temperature would not increase uniformly over the surface of the coated steel sheets (1), and therefore, the surface temperature would be of some uniformity. For this reason, it is preferred that, while temperature measurements being performed at a plurality of points or in a plurality of areas on the surface of the coated steel sheets (1) or over the whole surface thereof, the heating be performed until the lowest level of measurements reaches the blackening temperature. It is to be noted that, based upon the accumulated data having been obtained by measurements, it is also possible to set the heating conditions until the completion of heating without any actual temperature measurements.

[0037] The blackening temperature may be arbitrarily adjusted depending upon the composition (e.g., amounts of Al and Mg in the coating layer) or thickness of the coating layer, the required lightness, and so forth. The blackening temperature is preferably within a range of 50 °C to 350 °C, more preferably within a range of 105 °C to 200 °C. At a temperature above 105 °C, the blackening time could be shortened. At a temperature below 350 °C, the blackening device could be to be downsized, and the energy consumption required for heating steam and coated steel sheets (1) in blackening could be reduced, as well as the blackening degree of the coating layer could be easily controlled.

[0038] There are no particular restrictions on the heating method for the coated steel sheets (1) insofar as the surface of the coating layer could be heated until a resultant level reaches the blackening temperature. The coated steel sheets (1) may be heated in such a manner that, e.g., a heating device (24) such as a sheath heater installed in an interior of the sealable chamber (10) is configured to heat the atmospheric gas in the interior of the sealable chamber (10) so as to, through convection of such a heated gas, heat the coated steel sheets (1). Alternatively, the coated steel sheets (1) may be heated in such a manner such that, e.g., temperature regulation mechanisms (20, 21) installed on an exterior wall surface of the sealable chamber (10) is configured to regulate the temperature in the interior of the sealable chamber (10) so as to heat the coated steel sheets (1). Of course, the heating through either of the single use or the combination use of different means: a heating device (24) such as a sheath heater; and temperature regulation mechanisms (20, 21), may be adopted .

[0039] It is to be noted that a stirring device (70) such as a circulation fan (71) may be installed inside the sealable chamber (10) for stirring the atmospheric gas heated in the sealable chamber (10), which results in quick, effective, and uniform heating of the coated steel sheets (1).

[0040] (Second Step)

In the second step (S120), the atmospheric gas is discharged from the sealable chamber (10) through the gas discharge pipe (31) in order to reduce the gas pressure in the sealable chamber (10) to 70 kPa or lower. A gas discharge pump, e.g., (not shown) installed outside the sealable chamber (10) is configured to evacuate the sealable

chamber (10) for reducing an internal pressure of the atmospheric gas therein to fall within the above-described range. The discharge of the atmospheric gas in the second step (S120) may be performed on a one-time basis or more than one-time basis. In the latter case, the discharge of the atmospheric gas through the gas discharge pipe (31) from the sealable chamber (10) and the introduction of the low-steam gas through the gas introduction pipe (51) into the sealable chamber (10) may be performed in a repeated manner in order to further reduce the amount of the gas components other than steam remaining in the sealable chamber (10).

[0041] In an embodiment according to the present invention, the second step (S120) by which the atmospheric gas is discharged from the sealable chamber (10) to reduce the gas pressure therein so that steam, to be introduced in the third step (S130) as described later, could be distributed sufficiently around an interval area between the coated steel sheets (1), thereby enabling the more uniform steam treatment over the whole coating layer to be blackened, and enabling the reduction of non-uniform blackening. Furthermore, as a result of the evacuation in the second step (S120), an oxygen concentration in the sealable chamber (10) after the introduction of steam in the third step (S130) could be limited to 13% or lower. From these points of view, in the second step (S120), the gas pressure in the sealable chamber (10) is preferably 70 kPa or lower, and more preferably 50 kPa or lower.

[0042] (Third Step)

In the third step (S130), steam is introduced into the sealable chamber (10) so that the coating layer of the coated steel sheets (1) is blackened. In other words, in the third step (S130), the steam treatment is performed for the coated steel sheets (1).

[0043] In order to uniformly blacken the coated steel sheets (1), in the third step (S130), such blackening is preferably performed after having measured the temperatures at a plurality of points or in a plurality of areas on the surface of the coating layer, or over a whole surface of the coating layer so as to confirm that a difference between the highest and lowest measured values is lower than or equal to 30 °C, preferably lower than or equal to 20 °C, more preferably lower than or equal to 10 °C. In other words, it is preferred that the blackening in the third step (S130) be performed after the whole surface of the coated steel sheets (1) has a uniform temperature. In order to render the coated steel sheets (1) as having e.g. temperature differences on the surface thereof within the above-described range, an intermediate step as a surface-temperature uniformization step may be inserted between the first step (S110) and the second step (S120), or between the second step (S120) and the third step (S130), in which the coated steel sheets (1) are rendered at rest for allowing the coating layer to be uniformized in surface temperature.

[0044] In the third step (S130), an atmospheric temperature in the sealable chamber (10) during the steam treatment is preferably 105 °C or higher, and a relative humidity in the sealable chamber (10) during the steam treatment is within a range of 80% to 100%. By adjusting the atmospheric temperature to be above 105 °C as well as adjusting the relative humidity to be above 80%, the blackening could be performed within a shorter period of time. Further, at the atmospheric temperature above 105 °C, the coating layer could be blackened sufficiently, more specifically, lightness L of the coating layer in the

$L^*a^*b^*$  color space, e.g., could decrease in value below 60, preferably below 40, more preferably below 35. It is to be noted that lightness ( $L^*$  value) of the coating layer surface is obtained as a spectral reflectance detected by a spectral colorimeter. Still further, at the atmospheric temperature above 105 °C, the water condensation is not allowed to occur readily, and therefore, the occurrence of dew formation in the sealable chamber (10) and on the coating layer surface is suppressed. The atmospheric temperature is preferably within a range of 105 °C to 350 °C, more preferably within a range of 105 °C to 200 °C. The relative humidity is preferably 100%. The oxygen concentration in the sealable chamber (10) during the steam treatment is preferably 13% or lower. The oxygen concentration within this range could suppress non-uniform blackening. In the present specification, the temperature of atmospheric gas in the sealable chamber (10) will be referred to as "atmospheric temperature." The atmospheric temperature could be measured with a gas temperature measurement unit (62) installed in the sealable chamber (10).

[0045] Furthermore, during the steam treatment in the third step (S130), the interior of the sealable chamber (10) may be heated to maintain the above-described atmospheric temperature. There are no particular restrictions on the heating method insofar as the atmospheric temperature and relative humidity in the sealable chamber (10) could be regulated within the above-described ranges, respectively. For heating, e.g., temperature regulation mechanisms (20, 21), or a heating device (24) such as a sheath heater installed in the sealable chamber (10) may be used. The interior of the sealable chamber (10) may also be heated through the heated steam introduced into the interior.

[0046] Even with the aid of the present technologies, a direct measurement of relative humidity, dew point, or steam partial pressure itself in an atmosphere, whose temperature is higher than 100 °C, could hardly be performed. In the third step (S130), the atmosphere in the sealable chamber (10), immediately after starting the introduction of steam, consists completely of steam. For this reason, the relative humidity in the sealable chamber (10) is obtained by dividing the pressure value acquired as a result of a pressure gauge (61)'s measurements in the sealable chamber (10) by the saturated water vapor pressure acquired as a known value at the temperature. Once the blackening of the coating layer is started, however, the metal of the coating layer reacts with the steam to produce oxides and hydroxides as well as gaseous hydrogen regarded as being a by-product. As a result, the value of a total pressure acquired through the use of the pressure gauge (61; pressure measurement unit) is the sum of steam and hydrogen partial pressures. In other words, even if steam is introduced to maintain a predetermined total pressure, a problem occurs that a value of the actual relative humidity may be lower than the end value of the above-described preferable range due to the phenomenon where the generated gaseous hydrogen is present in the atmospheric gas in the sealable chamber (10) during the steam treatment.

[0047] In other words, Zinc (Zn) reacts with steam to produce Zn oxides or hydroxides and gaseous hydrogen generated at the same time. The overall reaction would presumably be expressed by formulas [1], [2] shown below. A problem occurs that the generated gaseous hydrogen accumulates in the sealable chamber (10), and the amount of the relative humidity decreases in the presence of such gaseous hydrogen along with steam. It is the present inventors' belief that, in the sealable chamber (10) whose

limited space has such phenomena occurring, the coating layer could not have any opportunities to sufficiently contact with steam, which results in non-uniform appearance of the black coated steel sheets (1).

Formula [1]:  $\text{Zn} + \text{H}_2\text{O} \rightarrow \text{ZnO} + \text{H}_2$

Formula [2]:  $\text{Zn} + 2\text{H}_2\text{O} \rightarrow \text{Zn}(\text{OH})_2 + \text{H}_2$

[0048] For solving the above-described problem so as to maintain an appropriate relative humidity, in the third step (S130) as an embodiment according to the present invention, steam is introduced into the sealable chamber (10), and thereafter, a certain amount of atmospheric gas is discharged from the sealable chamber (10), as well as, steam is further introduced into the sealable chamber (10). In other words, as a result of discharge of a certain amount of atmospheric gas accompanied by further introduction of steam, the atmospheric gas containing the hydrogen gas generated in the sealable chamber (10) could be discharged from the sealable chamber (10) in the third step (S130). As the above-configured, hydrogen gas is removed from the sealable chamber (10), and therefore, a total pressure in the sealable chamber (10) does not include any partial pressure of the generated hydrogen but consists solely of a pressure of saturated water vapor. Therefore, a value of the appropriate relative humidity could be obtained as a result of dividing a total pressure value in the sealable chamber (10) by the saturated water vapor pressure at the temperature.

[0049] Furthermore, if the atmospheric gas is discharged so that no hydrogen gas remains in the sealable chamber (10), there is a single component system of water (water vapor) in the sealable chamber (10), and the total pressure and the temperature in the sealable chamber (10) are not in a relation of independent variables from each other but in a relation of one variable to be determined uniquely by the other variable; in other words, the saturated vapor pressure is determined uniquely by the saturated vapor temperature, and alternatively, the saturated vapor temperature is determined uniquely by the saturated vapor pressure. The advantage of such a relation is in the ease of control; more specifically, one has only to be selected from the total pressure and the temperature in the sealable chamber (10) as a result of comparison in controllability between the two. Therefore, the generated hydrogen gas could be securely discharged in an efficient manner without any complicated management of the steam treatment in the manufacturing process, while steam could be distributed sufficiently around a whole area of the coated steel sheets, thereby capable of blackening uniformly the coating layer so as to manufacture the black coated steel sheets of further enhanced appearance.

[0050] It is to be noted that, if the reaction of formula [1] described above occurs in the blackening, 1 mol of steam is consumed in the reaction to produce 1 mol of hydrogen gas, without any change in the gas volume. In other words, by controlling the introduction of steam and the discharge of atmospheric gas in such a manner that the total pressure is maintained at a certain value in the sealable chamber (10), the generated hydrogen gas is discharged almost completely based upon the relationship of formula [3] shown below.

Formula [3]: "Amount of steam introduced into the sealable chamber" = "Net amount of discharged steam" + "Amount of generated hydrogen gas"

[0051] Further, if the reaction of formula [2] described above occurs, 2 mol of steam is consumed in the reaction to produce 1 mol of hydrogen gas, resulting in some decrease in the gas volume and some reduction in the internal pressure of the sealable chamber (10) but still securing the required amount of steam for blackening the coating layer. In other words, even if the set pressure is reduced to 80% thereof in the sealable chamber (10), such a negative pressure still allows discharging the generated hydrogen gas and supplying the required amount of steam for blackening the coating layer.

[0052] Still further, the reaction of formula [1] described above is exothermic. There are probabilities, therefore, that the internal temperature of the sealable chamber (10) during the steam treatment would exceed the set blackening temperature. The higher the temperature is, the higher the saturated water vapor pressure is. Based upon such principle, depending upon the internal temperature of the sealable chamber (10), the pressure could be raised to an extent of 120% of the set pressure so as to supply a sufficient amount of steam for blackening the coating layer.

[0053] Therefore, the internal pressure of the sealable chamber (10) during the steam treatment is preferably regulated within a range of 80% to 120% of the predetermined value of the set pressure.

[0054] Further, the discharge of atmospheric gas and the introduction of steam may be performed continuously throughout the third step (S130), more specifically, from the start to the completion in the step. Alternatively, they may be performed on a one-time basis in the step, or more than one-time basis at certain intervals in the step.

[0055] Still further, the atmospheric gas in the sealable chamber (10) may be stirred by a stirring unit (70) during the blackening after having introduced or while introducing steam into the sealable chamber (10) to prevent non-uniform blackening of the coated steel sheets (1).

[0056] Still further, a steam treatment time may be arbitrarily adjusted depending upon the composition (e.g., amounts of Al and Mg in the coating layer) or thickness of the coating layer, the required lightness, and so forth. However, the steam treatment time is preferably 24 hours or so.

[0057] In an embodiment according to the present invention, the amount of steam to be introduced into the sealable chamber (10) and the amount of atmospheric gas to be discharged from the sealable chamber (10) are adjustable. As shown in FIG. 2, the amount of steam in the sealable chamber (10) for blackening the coating layer is regulated by a steam introduction regulation mechanism (40) configured to adjust the amount of steam to be introduced into the sealable chamber (10), and a gas discharge regulation mechanism (30) configured to adjust the amount of atmospheric gas to be discharged from the sealable chamber (10), so as to maintain a predetermined pressure. More specifically, these regulation mechanisms (30, 40) are provided with pipes with different nominal diameters (20A, 25A, 80A), and these pipes are provided with gas discharge valves (322, 324, 326) (all of which will be, hereafter, collectively referred to as "gas discharge valves (32)") and steam supply valves (422, 424, 426) (all of which will be, hereinafter, collectively referred to as "steam supply valves (42)"), where these valves (32,



34) are so controlled as to be opened and closed by a control unit (90), which will be described later, to adjust the amount of steam to be introduced and the amount of atmospheric gas to be discharged, thereby maintaining the internal pressure at an appropriate value in the sealable chamber (10).

[0058] In an embodiment according to the present invention, the amount of steam in the sealable chamber (10) is adjusted as follows. The required amount of steam for blackening is determined by a surface area of the coated steel sheets (1) arranged in the sealable chamber (10). In order to secure the required amount of steam in the sealable chamber (10), the gas discharge valves (32) of the gas discharge regulation mechanism (30) are in the positions of their predetermined degrees of opening, while the steam supply valves (42) of the steam introduction regulation mechanism (40) are in the positions of their variably controllable degrees of opening. It is to be noted that such setting in degree of opening is not limited to the only possible setting, and that the steam supply valves (42) of the steam introduction regulation mechanism (40) may be in the positions of their predetermined degrees of opening, while the gas discharge valves (32) of the gas discharge regulation mechanism (30) may be in the positions of their variably controllable degrees of opening. Furthermore, the gas discharge valves (32) of the gas discharge regulation mechanism (30) and the steam supply valves (42) of the steam introduction regulation mechanism (40), both may be controlled in their opening positions at appropriate times.

[0059] Furthermore, due to the exothermic reaction of formula [1] described above, it is considered that the temperature of the coated steel sheets (1) increases with proceeding of the blackening. If the internal pressure of the sealable chamber (10) continues to remain at a predetermined value, the coated steel sheets (1) are subjected to the reduced relative humidity, which is unfavorable for quick blackening. Against such a matter, the gas discharge valves (32) of the gas discharge regulation mechanism (30) and/or the steam supply valves (42) of the steam introduction regulation mechanism (40) are in the positions of their respective degrees of opening so adjusted as to introduce a larger amount of steam into the sealable chamber (10), while the internal pressure of the sealable chamber (10) being maintained at a predetermined value, thereby enhancing the relative humidity for the coated steel sheets (1) so as to allow the blackening to proceed.

[0060] (Fourth Step)

In the fourth step (S140), the internal pressure of the sealable chamber (10) is returned to a value of the outside air pressure, and thereafter, the atmospheric gas is discharged from the sealable chamber (10) so as to reduce the gas pressure therein to 70 kPa or lower. In order to return the internal pressure of the sealable chamber (10) to a value of the outside air pressure, e.g., an outside air admittance valve (not shown) provided to the sealable chamber (10) is opened. Furthermore, in order to reduce the gas pressure in the sealable chamber (10) to 70 kPa or lower, the atmospheric gas is discharged from the sealable chamber (10), through the gas discharge pipe (31), by a gas discharge pump (not shown) installed outside the sealable chamber (10) configured to evacuate the sealable chamber (10).

[0061] In the fifth step (S150), which will be described later, if the coated steel sheets (1) are heated in the presence of remaining steam in the sealable chamber (10), there are

probabilities that the steam remaining in some gaps among the coated steel sheets (1) or elsewhere would be condensed, and the surface of the coated steel sheets (1) or the interior of the sealable chamber (10) would be subjected to the dew condensation. The coated steel sheets (1) having a surface on which such dew condensation occurs are adhered with water on the surface, and there are probabilities that the coated steel sheets (1) would have non-uniform blackening on their surface. Against such a matter, in the fourth step (S140), the internal pressure of the sealable chamber (10) is returned to a value of the outside air pressure, and thereafter, the atmospheric gas is discharged from the sealable chamber (10) so as to reduce the amount of steam in the sealable chamber (10). This prevents the above-described problem from occurring when the coated steel sheets (1) are cooled in the fifth step (S150). From the viewpoint of such circumstances, in the fourth step (S140), the gas pressure in the sealable chamber (10) is preferably reduced to 70 kPa or lower, more preferably to 30 kPa or lower.

[0062] (Fifth Step)

In the fifth step (S150), the coated steel sheets (1) are cooled in the presence of gas, whose dew point is lower than the temperature of the coated steel sheets at all times (low-steam gas), introduced through the gas introduction pipe (51) into the sealable chamber (10). The gas to be introduced, in the fifth step (S150), is preferably unheated, and may be heated, if necessary, to such an extent that its temperature does is lower than the atmospheric temperature inside the sealable chamber (10).

[0063] The low-steam gas to be introduced into the sealable chamber (10), in the fifth step (S150), may be, e.g., outside air, nitrogen gas, or inert gas. In view of workability, the sealable chamber (10) is preferably configured to admit the outside air therein.

[0064] Furthermore, the temperature of the atmospheric gas in the sealable chamber (10) may be lowered, if necessary, through the use of the temperature regulation mechanisms (20, 21) so as to cool the coated steel sheets (1).

[0065] It is to be noted that, through the use of the stirring device (70) such as a circulation fan (71) installed inside the sealable chamber (10) for cooling the atmospheric gas in the chamber, the coated steel sheets (1) could be cooled in a quick, effective, and uniform manner.

[0066] [Device for Manufacturing Black Coated Steel Sheets]  
(Structure of Device)

The device for manufacturing black coated steel sheets according to the present invention (which will be, hereinafter, occasionally referred to as the “device according to the present invention”), whose schematic cross-sectional view of an example is shown in FIG. 2, includes: a sealable chamber (10) including an arrangement portion (12) for arranging coated steel sheets (1) therein in a removable manner; a ceiling temperature regulation mechanism (21), a vertical wall temperature regulation mechanism (20), and a heating device (24), such as a sheath heater for heating (or cooling) an interior of the sealable chamber (10); a gas discharge regulation mechanism (30) configured to discharge atmospheric gas from the sealable chamber (10); and a steam introduction regulation mechanism (40) configured to introduce steam into the sealable chamber (10).

Further, the device according to the present invention may include: a gas

introduction unit (50) for introducing into the sealable chamber (10) gas containing outside air; and an outside air admittance valve (not shown) for returning the internal pressure of the sealable chamber (10) to a value of the outside air pressure.

Still further, the device according to the present invention may include: a temperature measurement unit (60) configured to measure the temperature of the coated steel sheets (1); a pressure measurement unit (61) configured to measure the internal pressure of the sealable chamber (10); a gas temperature measurement unit (62) configured to measure the temperature of the atmospheric gas; and a stirring unit (70) having a circulation fan (71) and the like configured to stir the atmospheric gas in the sealable chamber (10).

As shown in FIG. 3, the device according to the present invention may include: a control unit (90) configured to control the temperature regulation mechanisms (20, 21), the heating device (24) such as the sheath heater, the gas discharge regulation mechanism (30), the steam introduction regulation mechanism (40), the gas introduction unit (50), and the stirring unit (70), and in addition to them, the control unit (90) is configured to control the opening and closing of each valve in manufacturing the black coated steel sheets (1).

If the device according to the present invention further includes a drain pipe (35) and a drain valve (36), the control unit (90) may control the drain valve (36) to drain water from the device.

[0067] Hereinafter, an example of the device according to the present invention will be described with reference to the drawings, FIG. 2.

[0068] The sealable chamber (10) has a bottom frame (8) and an upper cover (9). The bottom frame (8) has the arrangement portion (12) for arranging the coated steel sheets (1) inside the sealable chamber. The upper cover (9) has an upper-cover ceiling portion (13) formed in a dome-like shape for a ceiling surface and an upper-cover vertical wall portion (14) formed in a cylindrical shape for a side surface. This upper cover (9) is configured in such a shape that a bottom side is opened.

Further, the sealable chamber (10) has the temperature regulation mechanisms (21, 20) independently provided on an exterior wall surface thereof, the ceiling temperature regulation mechanism (21) and the vertical wall temperature regulation mechanism (20), capable of heating and cooling, through a fluid-flow, an interior of the sealable chamber (10). In case that the interior of the sealable chamber (10) is cooled through the cooling of the upper-cover ceiling portion (13) by the ceiling temperature regulation mechanism (21), there are probabilities that an inner surface of the upper-cover ceiling portion (13) would be subjected to dew formation, and as a result, the water condensation would fall onto the coated steel sheets (1) to spoil their appearance. For this reason, the interior of the sealable chamber (10) is not cooled by the ceiling temperature regulation mechanism (21) but cooled by the vertical wall temperature regulation mechanism (20).

Still further, the sealable chamber (10) is defined by gas-tightly sealing between the bottom frame (8) and the upper cover (9), and is of strength enough to withstand the internal pressure decrease caused by discharging atmospheric gas, the internal pressure increase caused by introducing steam, the heating and cooling, and the like.

[0069] The bottom frame (8) is connected with: the steam supply pipe (41) for

introducing steam from a steam supply source; the gas discharge pipe (31) for discharging atmospheric gas and steam from the sealable chamber (10); the gas introduction pipe (51); the drain pipe (35). By closing the valves provided on these pipes, the interior of the sealable chamber (10) could be in a closed state.

[0070] The arrangement portion (12), which is installed on the bottom frame (8), is configured to allow the coated steel sheets (1) to be arranged thereon. The coated steel sheets (1) may be stacked with spacers (2) interposed between them. As shown in FIG. 2, the arrangement portion (12) has through holes (12A) formed to allow the atmospheric gas to pass from an upper side to a lower side of the coated steel sheets (1) so as to expel the atmospheric gas toward the circulation fan (71). Because of such a configuration, the gas in the sealable chamber (10) passes through the gaps between metallic bands of the coated steel sheets (1) for circulation. As a result, the coated steel sheets (1) could allow the atmospheric gas to have more uniform contact therewith.

[0071] The gas discharge regulation mechanism (30) includes the gas discharge pipe (31), gas discharge valves (32), and gas discharge pump (not shown). The gas discharge pipe (31) is a pipe formed on an outer side of the bottom frame (8) to pass through the bottom frame (8) between its outer and inner sides so that the inside and outside of the sealable chamber (10) could communicate with each other. For example, the atmospheric gas (low-steam gas, etc.) in the sealable chamber (10), or the atmospheric gas (steam, generated hydrogen gas, etc.) in the sealable chamber (10) after the steam treatment, is discharged to the outside through the gas discharge pipe (31) with the help of the gas discharge pump (not shown). In an embodiment according to the present invention, as shown in FIG. 2, the gas discharge pipe (31) is connected to pipes (332, 334, 336) having different nominal diameters from each other so as to adjust the amount of steam in the sealable chamber (10) during the steam treatment. These pipes have their respective gas discharge valves (32) provided thereon. For example, the valves (32) of three pipes (332, 334, 336) with nominal diameters of 20A, 25A, 80A, respectively, could be opened and closed by the control unit (90), which will be described later, for accurate and precise gas discharge regulation in response to the required amount of steam in the sealable chamber (10). This is not limited to the only possible embodiment, and the number and nominal diameters of the pipes (332, 334, 336) could be altered for any specific needs. In the above-described second and fourth steps, the gas discharge regulation mechanism (30) is configured to discharge the atmospheric gas thereby adjusting the gas pressure in the sealable chamber (10) to 70 kPa or lower.

[0072] The drain pipe (35) is a pipe formed on an outer side of the bottom frame (8) to pass through the bottom frame (8) between its outer and inner sides so that the inside and outside of the sealable chamber (10) could communicate with each other. The fluid (dew, etc.) in the sealable chamber (10) could be drained to the outside through this drain pipe (35).

[0073] The steam introduction regulation mechanism (40) includes the steam supply pipe (41) and steam supply valves (42), for adjusting the amount of steam to be supplied to the sealable chamber (10). When the steam introduction regulation mechanism (40) is in a mode of not supplying steam, the steam supply valves (42) are closed to prevent steam from being supplied to the sealable chamber (10) through the steam supply pipe

(41). In the device for manufacturing black coated steel sheets in an embodiment according to the present invention, as shown in FIG. 2, the steam supply pipe (41) is connected to pipes (432, 434, 436) having different nominal diameters from each other. The pipes have their respective steam supply valves (42) provided thereon. For example, the valves (42) of three pipes (432, 434, 436) with nominal diameters of 20A, 25A, 80A, respectively, could be opened and closed by control for accurate and precise steam introduction regulation in response to the required amount of steam in the sealable chamber (10). This is not limited to the only possible embodiment, and the number and nominal diameters of the pipes (432, 434, 436) could be altered for any specific needs.

[0074] The gas introduction unit (50) has the gas introduction pipe (51) and a gas introduction valve (52). The gas introduction pipe (51) is a pipe formed on an outer side of the bottom frame (8) to pass through the bottom frame (8) between its outer and inner sides so that the inside and outside of the sealable chamber (10) could communicate with each other, or the inside of the sealable chamber (10) and a gas supply source (not shown) could communicate with each other. For example, in the above-described first and fifth steps (S110, S150), the gas introduction unit (50) could be used for introducing low-steam gas into the sealable chamber (10).

[0075] The temperature measurement unit (60) includes a plurality of temperature sensors set in contact with different areas on the surface of the coated steel sheets (1) configured to detect the temperatures of the coated steel sheets (1), for example, serving as thermocouples. When the coated steel sheets (1) are in coil form, the thermocouples may be inserted between the sheets in coil form.

[0076] The pressure measurement unit (61) is configured to measure the internal pressure of the sealable chamber (10). This unit includes a pressure gauge configured to detect a gauge pressure in the first, third, fifth steps (S110, S130, S150), and a vacuum gauge configured to detect a pressure lower in value than the outside air pressure in the second, fourth steps (S120, S140). These gauges may be used, in a switchable manner, between them.

[0077] The gas temperature measurement unit (62) includes a temperature sensor configured to detect the temperature of the atmospheric gas in the sealable chamber (10). For example, a thermocouple may be used for the temperature sensor. In place of one sensor placed at one point of the interior of the sealable chamber (10), a plurality of sensors placed at a plurality of points of the interior may be used, in an appropriately switchable manner, among them.

[0078] The stirring unit (70) includes the circulation fan (71) arranged with respect to the bottom frame (8), and a drive motor (72) configured to rotate the circulation fan (71).

When the drive motor (72) rotates the circulation fan (71), the atmospheric gas in the sealable chamber (10) during the steam treatment, as shown by the arrows in FIG. 2, is allowed to: flow from a lateral side of the arrangement portion (12) into a gap between the lateral side and an interior wall surface of the sealable chamber (10); pass along an outer peripheral surface of the coated steel sheets (1); and then flow into gaps between metallic bands from an upper side of the coated steel sheets (1); and thereafter, flow from a lower side of the coated steel sheets (1) into an interior of the arrangement portion

(12); and again flow from the lateral side of the arrangement portion (12) into the gap between the lateral side and the interior wall surface of the sealable chamber (10), for circulation in the sealable chamber (10).

In such a manner, the atmospheric gas in the sealable chamber (10) during the steam treatment is stirred. The stirring unit (70) may be used not only during the steam treatment but also in the heating and cooling of the coated steel sheets (1).

#### [0079] [System for Manufacturing Black Coated Steel Sheets]

Hereinafter, an exemplary operation of the device for manufacturing black coated steel sheets according to the present invention and its control system will be described with reference to the drawings, FIG. 3.

[0080] After the coated steel sheets (1) are arranged in the arrangement portion (12) and the sealable chamber (10) is closed, the control unit (90) exerts the controls, which will be described below, of the operations of the temperature regulation mechanisms (20, 21), the heating device (24) such as a sheath heater, the gas discharge regulation mechanism (30), the steam introduction regulation mechanism (40), the gas introduction unit (50), and the stirring unit (70).

[0081] In the first step of heating the coated steel sheets (1), the control unit (90) causes the temperature regulation mechanisms (20, 21) and/or the heating device (24) such as a sheath heater to heat the interior of the sealable chamber (10) and, as a result, heat the coated steel sheets (1) in the presence of the low-steam gas. In the heating, the control unit (90) causes each of the above heating means to operate until the temperature of the coating layer measured by the temperature measurement unit (60) reaches a level of the blackening temperature. It is to be noted that, in an embodiment according to the present invention, a target blackening temperature is set to be 105 °C. The control of heating may be exerted, if necessary, while the circulation fan (71) being rotated so as to circulate the atmospheric gas in the sealable chamber (10).

[0082] In the second step subsequent to the completion of the first step, the control unit (90) causes the gas discharge regulation mechanism (30) to open the gas discharge valves (32) and energize the gas discharge pump (not shown) to operate, so as to discharge the atmospheric gas from the sealable chamber (10) through the gas discharge pipe (31) until the gas pressure in the sealable chamber (10) decreases to 70 kPa or lower. When the measured value of gas pressure in the sealable chamber (10) is equal to or lower than 70 kPa, the control unit (90) closes the gas discharge valves (32). It is to be noted that, before opening the gas discharge valves (32) and energizing the gas discharge pump of the gas discharge regulation mechanism (30), an outside air admittance valve (not shown) may be opened to return the internal pressure of the sealable chamber (10) to a value of the outside air pressure.

[0083] In the third step subsequent to a timing of the internal gas pressure reaching the above-described pressure value, the control unit (90) causes the steam introduction regulation mechanism (40) to open the steam supply valves (42) thereby to supply steam to the sealable chamber (10) from a steam supply source. As a result, steam is introduced into the sealable chamber (10) through the steam supply pipe (41). The steam supply valves (42) may be opened by the steam introduction regulation mechanism

(40) on the basis of a result of determination, by the control unit (90), that a difference between the maximum and minimum out of a plurality of temperatures measured by the plurality of temperature sensors of the temperature measurement unit (60) falls within the predetermined range described above. If necessary, steam to be introduced may be heated with a steam heater (not shown).

[0084] Furthermore, if necessary, the control unit (90) may cause the stirring unit (70) to energize the drive motor (72) to rotate the circulation fan (71) thereby to stir and circulate the atmospheric gas containing steam in the sealable chamber (10).

[0085] It is to be noted that, in an embodiment according to the present invention, the control unit (90) is configured to cause the steam introduction regulation mechanism (40) to adjust the amount of steam to be introduced into the sealable chamber (10), and the gas discharge regulation mechanism (30) to adjust the amount of atmospheric gas to be discharged from the sealable chamber (10), thereby to adjust at all times the required amount of steam in the sealable chamber (10) for blackening the coating layer, remove appropriately the hydrogen gas generated in the sealable chamber (10), and maintain an appropriate relative humidity (a target value is 100%). More specifically, the control unit (90) causes the above-described regulation mechanisms (30, 40) to open/close each of the gas discharge valves (32) and the steam supply valves (42) provided on the pipes with their respective nominal diameters different from each other, thereby adjusting the amount of steam to be introduced and the amount of atmospheric gas to be discharged.

[0086] The amount of steam required for blackening is in principle determined by a surface area of the coated steel sheets (1). When adjusting the amount of steam in the sealable chamber (10), the control unit (90) sets the gas discharge valves (32) of the gas discharge regulation mechanism (30) to be in positions of their predetermined degrees of opening, and adjusts the steam supply valves (42) of the steam introduction regulation mechanism (40) to be in positions of their variable degrees of opening, so that the required amount of steam could be secured in the sealable chamber (10). It is to be noted that the steam supply valves (42) of the steam introduction regulation mechanism (40) may be in the positions of their predetermined degrees of opening, while the gas discharge valves (32) of the gas discharge regulation mechanism (30) may be in the positions of their variably controllable degrees of opening, or that the gas discharge valves (32) of the gas discharge regulation mechanism (30) and the steam supply valves (42) of the steam introduction regulation mechanism (40), both may be controlled in their opening positions at appropriate times.

[0087] When adjusting the introduction of steam into the sealable chamber (10) and the discharge of atmospheric gas (steam, hydrogen gas generated in the reaction, etc.) from the sealable chamber (10), the control unit (90) reads, at all times, the data acquired as a result of the measurements by the pressure measurement unit (61) in order to maintain a required pressure in the sealable chamber (10) so that the required amount of steam for the steam treatment could be secured in the sealable chamber (10). It is to be noted that, in an embodiment according to the present invention, the internal pressure of the sealable chamber (10) during the steam treatment is set to be 121 kPa, through the control unit (90), as the saturated water vapor pressure corresponding to a temperature, 105 °C, in the sealable chamber (10). Further, as to how to adjust the internal pressure

of the sealable chamber (10), when it is determined by the control unit (90) that the measured value of the internal pressure is equal to or higher than a predetermined threshold value set between the maximum and minimum out of a plurality of pieces of data acquired by the pressure measurement unit (61), the amount of steam to be introduced and the amount of steam to be discharged may be adjusted. Otherwise, the amount of steam to be introduced and the amount of steam to be discharged may be adjusted, at appropriate time, in such a manner that, at all time, the measured value of the internal pressure is maintained at a certain value.

[0088] When a period of time for the blackening elapses after the introduction of steam, the control unit (90) causes the steam introduction regulation mechanism (40) to close the steam supply valves (42) so as to cutoff a gas flow through the steam supply pipe (41) between the inside and outside of the sealable chamber (10), and thereafter, causes the gas discharge regulation mechanism (30) to open the gas discharge valves (32) and energize the gas discharge pump (not shown) to operate, so as to discharge the atmospheric gas from the sealable chamber (10), thereby reducing the gas pressure in the sealable chamber (10) to 70 kPa or lower. When the measured value of gas pressure in the sealable chamber (10) is equal to or lower than 70 kPa, the control unit (90) causes the gas discharge regulation mechanism (30) to open the gas discharge valves (32) so as to cutoff a gas flow through the gas discharge pipe (31) between the inside and outside of the sealable chamber (10).

[0089] In the fifth step subsequent to a timing of the internal gas pressure reaching the above-described pressure value, the control unit (90) causes the gas introduction unit (50) to open the gas introduction valve (52) so as to introduce gas, whose dew point is lower than the temperature of the coated steel sheets (1) at all times, into the sealable chamber (10) through the gas introduction pipe (51). In an embodiment according to the present invention, the outside air is introduced until the gas pressure in the sealable chamber (10) reaches 101 kPa (substantially equal to a value of the outside air pressure). Through the introduced gas (outside air in this embodiment), the coated steel sheets (1) are cooled.

[0090] At any time, including a time when the coated steel sheets (1) are cooled, the control unit (90) may open the drain valve (36) to drain dew and the like from the sealable chamber (10). The control of the drain valve (36) may be performed on a one-time basis or more than one-time basis during the operation of the device according to the present invention, or the drain valve (36) may remain closed throughout the operation of the device insofar as the coating layer is blackened to the extent satisfactory.

[0091] (Effects)

According to the method as embodiments of the present invention, the hydrogen gas generated during the steam treatment could be securely discharged in an efficient manner without any complicated management of such steam treatment in the manufacturing process, while steam could be distributed sufficiently around a whole area of the coated steel sheets, thereby capable of blackening uniformly the coating layer, and as a result, the black coated steel sheets of further enhanced appearance could be provided.

[0092] (Industrial Applicability)



By the method according to the present invention, the hydrogen gas generated during the steam treatment of the coated steel sheets is discharged appropriately, and the appropriately-adjusted amount of steam for the steam treatment is supplied, thereby to manufacture more uniformly-blackened coated steel sheets of enhanced appearance, and be expected to contribute to further increased popularity of black coated steel sheets.

[0093] (Reference Numerals)

1 Coated steel sheets

10 Sealable chamber

[0094] Any reference herein to known prior art does not, unless the contrary indication appears, constitute an admission that such prior art is commonly known by those skilled in the art to which the invention relates, at the priority date of this application.

[0095] Where ever it is used, the word “comprising” is to be understood in its “open” sense, that is, in the sense of “including”, and thus not limited to its “closed” sense, that is the sense of “consisting only of”. A corresponding meaning is to be attributed to the corresponding words “comprise”, “comprised” and “comprises” where they appear.

## WHAT IS CLAIMED IS:

1. A method for manufacturing a black coated steel sheet by bringing steam into contact with a hot-dip Zn-Al-Mg alloy coated steel sheet under a closed atmosphere, the method comprising a step of,
  - in a sealable chamber configured such that an amount of steam flowing into the sealable chamber and an amount of atmospheric gas flowing out of the sealable chamber are variably controllable,
  - maintaining an internal pressure in the sealable chamber, while causing steam to flow into the sealable chamber through the use of a plurality of pipes, and causing atmospheric gas to flow out of the sealable chamber through the use of a plurality of pipes, in parallel with each other, so as to prohibit hydrogen gas generated in the sealable chamber from remaining therein, thereby to
  - allow contact to occur between: the hot-dip Zn-Al-Mg alloy coated steel sheet; and the steam introduced into the sealable chamber.
2. A method for manufacturing a black coated steel sheet by bringing steam into contact with a hot-dip Zn-Al-Mg alloy coated steel sheet under a closed atmosphere, the method comprising a step of,
  - in a sealable chamber configured such that at least one of an amount of steam flowing into the sealable chamber and an amount of atmospheric gas flowing out of the sealable chamber are variably controllable,
  - maintaining an internal pressure in the sealable chamber at between 80% and 120% of a predetermined value, while causing steam to flow into the sealable chamber through the use of a plurality of pipes, and causing atmospheric gas to flow out of the sealable chamber through the use of a plurality of pipes, in parallel with each other, through variable control of at least one of an amount of the steam flowing into the sealable chamber and an amount of the atmospheric gas flowing out of the sealable chamber, so as to prohibit hydrogen gas generated in the sealable chamber from remaining therein, thereby to
  - allow contact to occur between: the hot-dip Zn-Al-Mg alloy coated steel sheet; and the steam introduced into the sealable chamber.
3. A device for manufacturing a black coated steel sheet by performing treatment of bringing steam into contact with a hot-dip Zn-Al-Mg alloy coated steel sheet under a closed atmosphere, the device comprising:
  - a sealable chamber configured to allow the hot-dip Zn-Al-Mg alloy coated steel sheet to be arranged therein;
  - a plurality of introduction pipes for steam to flow into the sealable chamber;
  - a plurality of discharge pipes for atmospheric gas to flow out of the sealable chamber; and
  - a pressure control unit configured to variably control an amount of steam flowing into the sealable chamber through the plurality of introduction pipes, and to variably control an amount of atmospheric gas flowing out of the sealable chamber through the plurality of discharge pipes, so as to maintain an internal pressure in the sealable chamber at a predetermined value, wherein,
    - the pressure control unit is further configured to,
    - during treatment of bringing the steam into contact with the hot-dip Zn-Al-Mg

alloy coated steel sheet,

maintain the internal pressure in the sealable chamber, while

causing the steam to flow into the sealable chamber, and causing the atmospheric gas to flow out of the sealable chamber, in parallel with each other, so as to prohibit hydrogen gas generated in the sealable chamber from remaining therein.

4. A device for manufacturing a black coated steel sheet by performing treatment of bringing steam into contact with a hot-dip Zn-Al-Mg alloy coated steel sheet under a closed atmosphere, the device comprising

a sealable chamber configured to allow the hot-dip Zn-Al-Mg alloy coated steel sheet to be arranged therein;

a plurality of introduction pipes for steam to flow into the sealable chamber;

a plurality of discharge pipes for atmospheric gas to flow out of the sealable chamber; and

a pressure control unit configured to variably control at least one of an amount of steam flowing into the sealable chamber through the plurality of introduction pipes, and an amount of atmospheric gas flowing out of the sealable chamber through the plurality of discharge pipes, so as to maintain an internal pressure in the sealable chamber at a predetermined value, wherein

the pressure control unit is further configured to,

during treatment of bringing the steam into contact with the hot-dip Zn-Al-Mg alloy coated steel sheet,

maintain the internal pressure in the sealable chamber at between 80% and 120% of a predetermined value, while

causing the steam to flow into the sealable chamber, and causing the atmospheric gas to flow out of the sealable chamber, in parallel with each other, through variable control of at least one of an amount of the steam flowing into the sealable chamber and an amount of the atmospheric gas flowing out of the sealable chamber, so as to prohibit hydrogen gas generated in the sealable chamber from remaining therein.

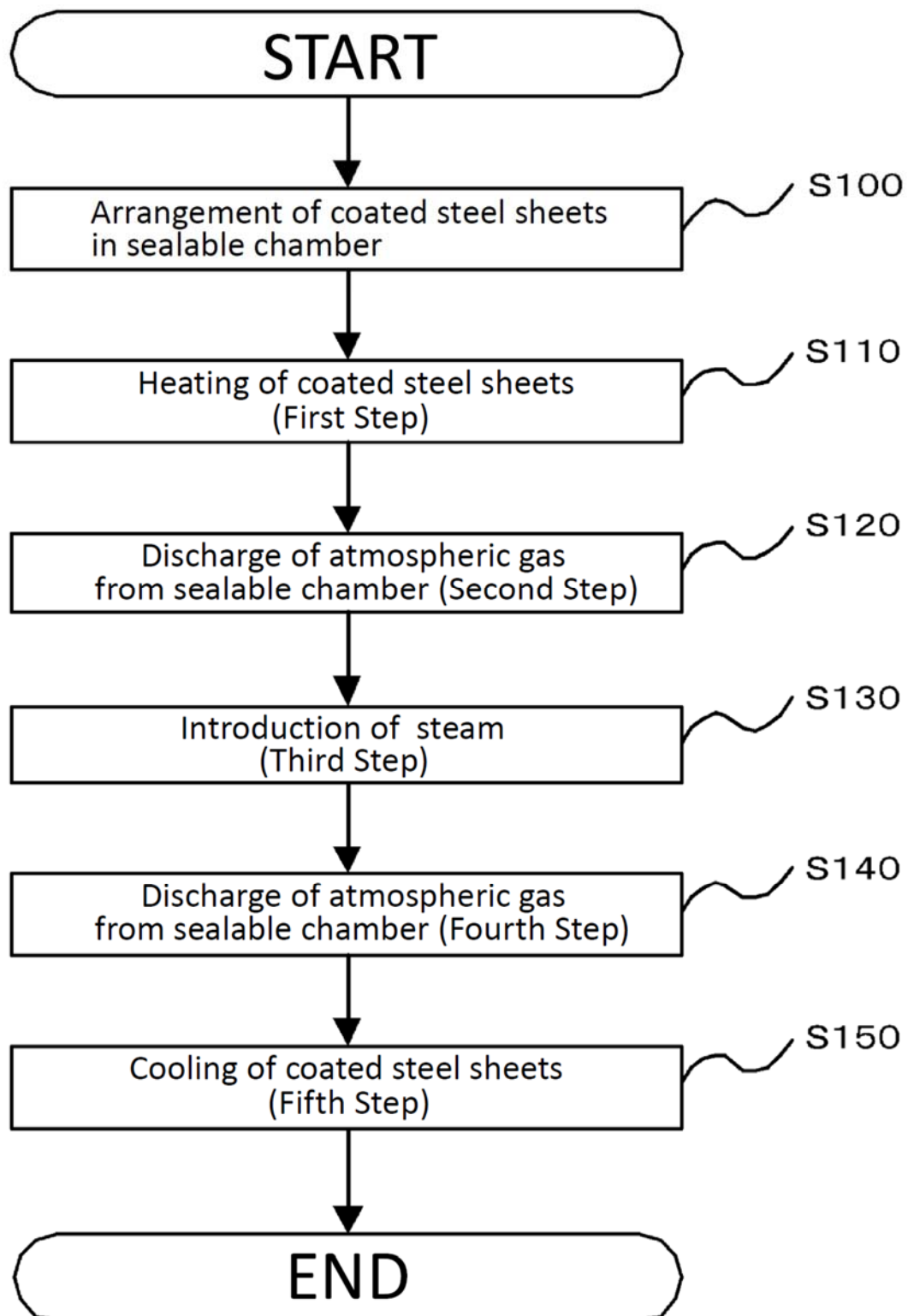


FIG. 1

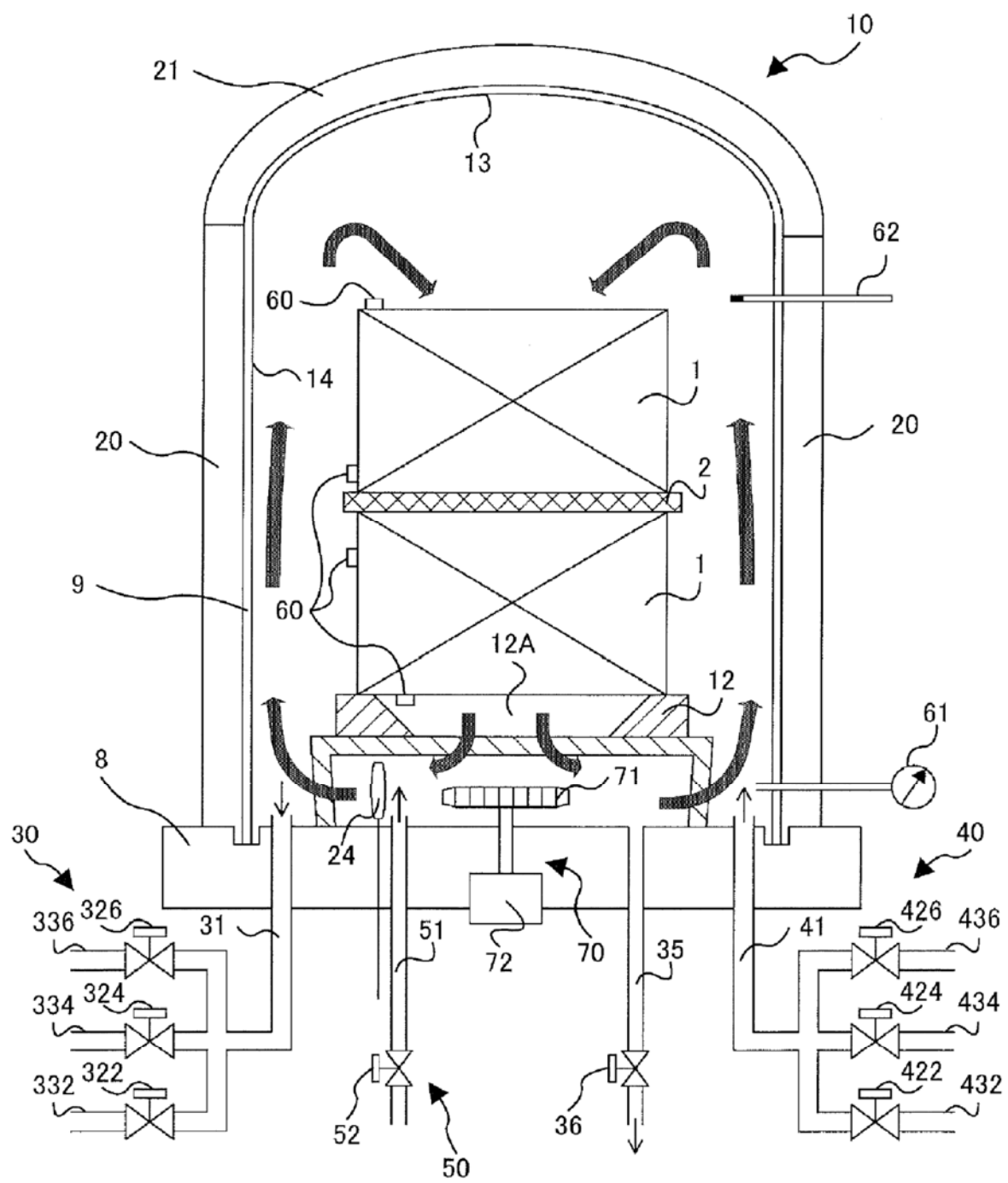


FIG. 2

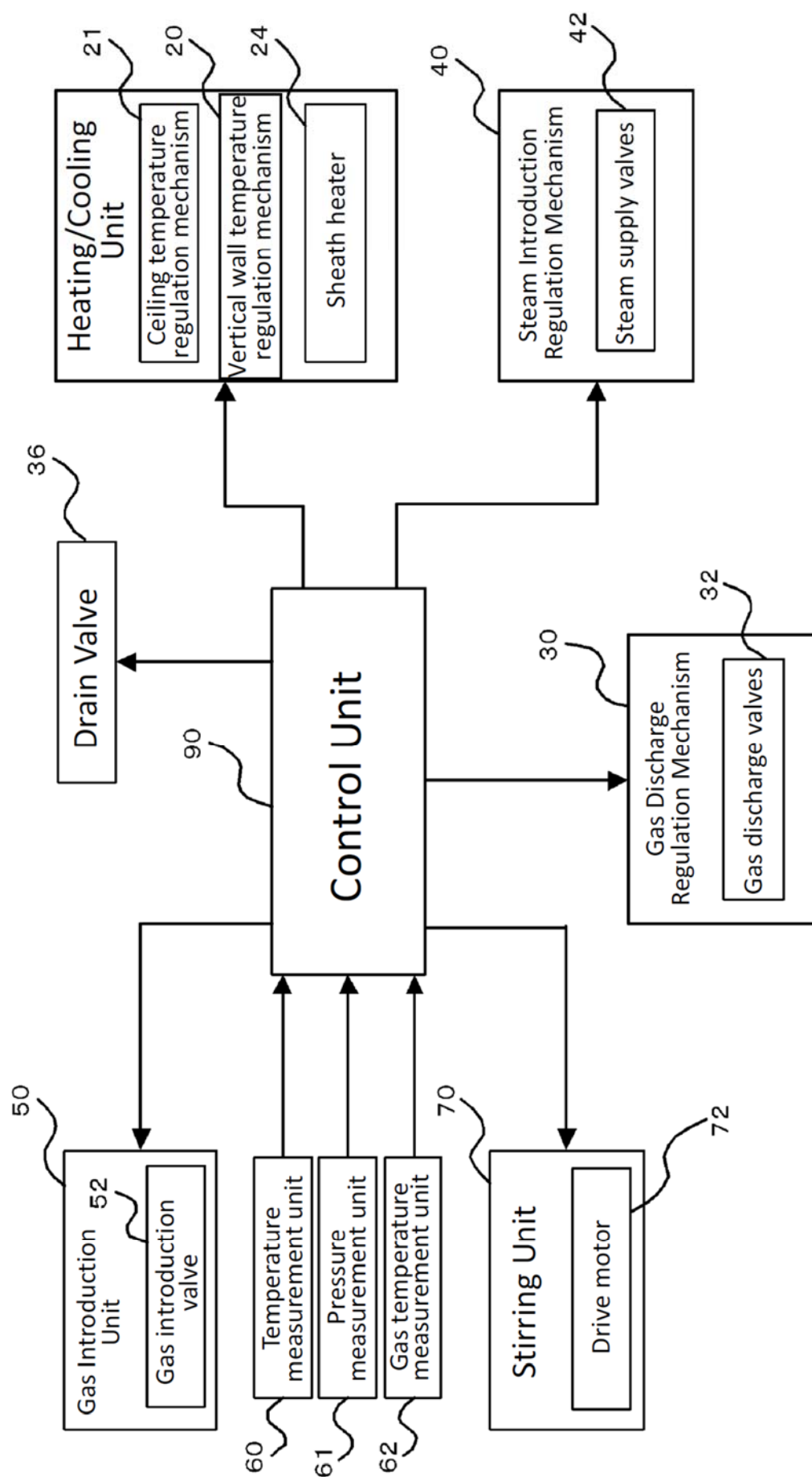


FIG. 3