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(54) FLUORINE GAS GENERATION DEVICE

(57) A refining device is provided to remove hydrogen fluoride gas that is vaporized from molten salt and intermixed into a main product gas. Two refining devices are disposed parallel to each other, each refining device includes a cooling device that cools a gas inflow portion such that the hydrogen fluoride gas coagulates while the fluorine gas passes through the gas inflow portion. A control device performs an operation changeover on the refining device on the basis of a detection result from an detector that detects an accumulation condition of the hydrogen fluoride in the gas inflow portion so that fluorine gas is led into a refining device on standby, and sets a refining device stopped by the operation changeover in a standby condition by discharging the hydrogen fluoride from the gas inflow portion of the stopped refining device and supplying fluorine gas to the gas inflow portion thereof.

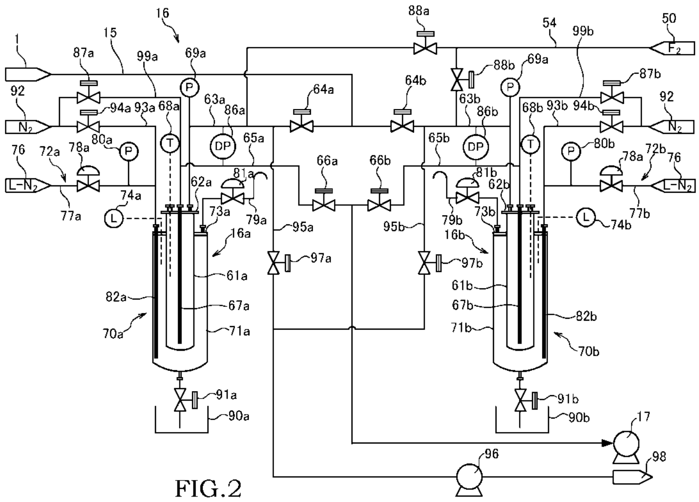

FIG.2

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Description

TECHNICAL FIELD

[0001] This invention relates to a fluorine gas generation device.

BACKGROUND ART

[0002] A device that generates fluorine gas through electrolysis using an electrolytic cell is known as a conventional fluorine gas generation device.

[0003] JP2004-43885A discloses a fluorine gas generation device comprising an electrolytic cell that electrolyzes hydrogen fluoride in an electrolyte constituted by molten salt containing hydrogen fluoride, in which a product gas having fluorine gas as a main component is generated in a first gas phase part on an anode side and a byproduct gas having hydrogen gas as a main component is generated in a second gas phase part on a cathode side.

[0004] In this type of fluorine gas generation device, hydrogen fluoride gas that vaporizes from the molten salt intermixes with the fluorine gas generated by an anode of the electrolytic cell. Therefore, the fluorine gas must be refined by separating the hydrogen fluoride from the gas generated by the anode.

[0005] JP2004-39740A discloses cooling a fluorine gas component and a component other than the fluorine gas component using liquid nitrogen or the like, and separating the fluorine gas using a difference between boiling points of the two components.

SUMMARY OF THE INVENTION

[0006] As described in JP2004-39740A, when the fluorine gas component is separated from the component other than fluorine gas component using the boiling point difference, the component other than the fluorine gas component coagulates during the cooling, and when a coagulation amount thereof equals or exceeds a predetermined amount, the entire fluorine gas generation device must be stopped in order to remove the coagulated component.

[0007] A time required to reactivate the fluorine gas generation device after stopping the device includes a time required to remove the coagulated component and a time required to reactivate the fluorine gas generation device, and therefore the fluorine gas generation device must be stopped for a considerable period. When the fluorine gas generation device is stopped, no fluorine gas can be supplied to an external device that consumes the fluorine gas.

[0008] Hence, when a device that separates a fluorine gas component from a component other than the fluorine gas component using a boiling point difference is employed, fluorine gas cannot be supplied to an external device with stability.

[0009] This invention has been designed in consideration of the problem described above, and an object thereof is to provide a fluorine gas generation device capable of supplying fluorine gas to an external device with stability.

[0010] This invention is a fluorine gas generation device that generates fluorine gas by electrolyzing hydrogen fluoride in molten salt. The fluorine gas generation device comprises an electrolytic cell storing the molten salt, in which a first gas chamber to which a main product gas having fluorine gas generated by an anode submerged in the molten salt as a main component is led and a second gas chamber to which a byproduct gas having hydrogen gas generated by a cathode submerged in the molten salt as a main component is led are separated and defined above a liquid level of the molten salt, a refining device that refines the fluorine gas by scavenging hydrogen fluoride gas that is vaporized from the molten salt in the electrolytic cell and intermixed into the main product gas generated by the anode, and a control device that controls an operation of the refining device, wherein at least two of the refining devices are disposed parallel to each other, each refining device comprises a gas inflow portion into which the main product gas containing the hydrogen fluoride gas flows, a cooling device that cools the gas inflow portion to a temperature equal to or higher than a boiling point of fluorine and equal to or lower than a melting point of hydrogen fluoride such that the hydrogen fluoride gas intermixed into the main product gas coagulates while the fluorine gas passes through the gas inflow portion, and an accumulation condition detector that detects an accumulation condition of the hydrogen fluoride in the gas inflow portion, and the control device performs an operation changeover on the refining device on the basis of a detection result from the accumulation condition detector so that fluorine gas is led into a refining device on standby, and sets a refining device stopped by the operation changeover in a standby condition by discharging the hydrogen fluoride from the gas inflow portion of the stopped refining device and supplying fluorine gas to the gas inflow portion thereof.

[0011] According to this invention, at least two refining devices are disposed parallel to each other, and a refining device that is stopped by an operation changeover is set in a standby condition by discharging hydrogen fluoride from a gas inflow portion and then supplying fluorine gas to the gas inflow portion. Thus the refining device on the standby condition can be operated at any time. Therefore, the refining device on the standby condition can be activated even when an accumulated amount of coagulated hydrogen fluoride in the operative refining device is large such that the refining device is stopped. Accordingly, the fluorine gas generation device itself need not be stopped, and therefore fluorine gas can be supplied to an external device with stability.

BRIEF DESCRIPTION OF THE DRAWINGS

[0012]

FIG. 1 is a system diagram of a fluorine gas generation device according to an embodiment of this invention.

FIG. 2 is a system diagram of a refining device.

FIG. 3 is a graph showing temporal variation in a pressure and a temperature in an inner tube of the refining device, wherein a solid line indicates the pressure and a dot-dash line indicates the temperature.

EMBODIMENT OF THE INVENTION

[0013] An embodiment of this invention will be described below with reference to the drawings.

[0014] Referring to FIG. 1, a fluorine gas generation device 100 according to a first embodiment of this invention will be described.

[0015] The fluorine gas generation device 100 generates fluorine gas through electrolysis and supplies the generated fluorine gas to an external device 4. The external device 4 may be a semiconductor manufacturing device, for example. In this case, the fluorine gas is used as a cleaning gas in a process for manufacturing a semiconductor, for example.

[0016] The fluorine gas generation device 100 includes an electrolytic cell 1 that generates fluorine gas through electrolysis, a fluorine gas supply system 2 that supplies the generated fluorine gas from the electrolytic cell 1 to the external device 4, and a byproduct gas processing system 3 that processes a byproduct gas generated during generation of the fluorine gas.

[0017] First, the electrolytic cell 1 will be described.

[0018] Molten salt containing hydrogen fluoride (HF) is stored in the electrolytic cell 1. In this embodiment, a mixture (KF-2HF) of hydrogen fluoride and potassium fluoride (KF) is used as the molten salt.

[0019] An interior of the electrolytic cell 1 is partitioned into an anode chamber 11 and a cathode chamber 12 by a partition wall 6 submerged in the molten salt. An anode 7 and a cathode 8 are submerged respectively in the molten salt in the anode chamber 11 and the cathode chamber 12. When a current is supplied between the anode 7 and the cathode 8 from a power supply 9, a main product gas having fluorine gas (F_2) as a main component is generated in the anode 7 and a byproduct gas having hydrogen gas (H_2) as a main component is generated in the cathode 8. A carbon electrode is used as the anode 7, and soft iron, monel metal, or nickel is used as the cathode 8.

[0020] A first gas chamber 11a to which the fluorine gas generated by the anode 7 is led and a second gas chamber 12a to which the hydrogen gas generated by the cathode 8 is led are defined above a molten salt liquid level in the electrolytic cell 1 by the partition wall 6 such that gas cannot pass there-between. The first gas chamber 11a and the second gas chamber 12a are completely separated by the partition wall 6, and therefore a reaction caused by intermixing between the fluorine gas and the hydrogen gas is prevented. The molten salt in the anode chamber 11 and the cathode chamber 12, on the other hand, passes under the partition wall 6, and therefore the anode chamber 11 and cathode chamber 12 communicate with each other without being separated by the partition wall 6.

[0021] The melting point of KF-2HF is 71.7°C, and therefore the temperature of the molten salt is regulated to 90 to 100°C. An amount of hydrogen fluoride corresponding to a vapor pressure vaporizes from the molten salt and intermixes with the fluorine gas and the hydrogen gas generated respectively from the anode 7 and the cathode 8 of the electrolytic cell 1. Accordingly, the fluorine gas generated in the anode 7 and led to the first gas chamber 11a and the hydrogen gas generated in the cathode 8 and led to the second gas chamber 12a respectively contain hydrogen fluoride gas.

[0022] A first pressure gauge 13 that detects a pressure in the first gas chamber 11a and a second pressure gauge 14 that detects a pressure in the second gas chamber 12a are provided in the electrolytic cell 1. Detection results from the first pressure gauge 13 and the second pressure gauge 14 are output to controllers 10a, 10b.

[0023] Next, the fluorine gas supply system 2 will be described.

[0024] A first main passage 15 for supplying the fluorine gas to the external device 4 is connected to the first gas chamber 11a.

[0025] A first pump 17 that suctions and conveys the fluorine gas from the first gas chamber 11a is provided in the first main passage 15. A positive displacement pump such as a bellows pump or a diaphragm pump is used as the first pump 17. A first recirculation passage 18 that connects a discharge side and a suction side of the first pump 17 is connected to the first main passage 15. A first pressure regulating valve 19 for returning fluorine gas discharged from the first pump 17 to the suction side of the first pump 17 is provided in the first recirculation passage 18.

[0026] An opening of the first pressure regulating valve 19 is controlled by a signal output from the controller 10a. More specifically, the controller 10a controls the opening of the first pressure regulating valve 19 on the basis of the detection result from the first pressure gauge 13 such that the pressure in the first gas chamber 11a reaches a predetermined set value.

[0027] It should be noted that in FIG. 1, a downstream end of the first recirculation passage 18 is connected to the first main passage 15 in the vicinity of the first pump 17, but the downstream end of the first recirculation passage 18 may be connected to the first gas chamber 11a. In other words, the fluorine gas discharged from the first pump 17 may be returned into the first gas chamber 11 a.

[0028] A refining device 16 that refines the fluorine gas by scavenging the hydrogen fluoride gas intermixed into the main product gas is provided in the first main passage 15 upstream of the first pump 17. The refining device 16 is a low temperature refining device that separates and removes the hydrogen fluoride gas from the fluorine gas using a difference in the boiling points of fluorine and hydrogen fluoride. The refining device 16 is constituted by two systems, namely a first refining device 16a and a second refining device 16b arranged parallel to each other, only one of which is operated such that fluorine gas can pass there-through. In other words, when one of the first refining device 16a and the second refining device 16b is operative, the other is stopped or on standby. It should be noted that in this embodiment, two refining devices 16 are arranged parallel to each other to form two systems, but three or more refining devices 16 may be arranged parallel to each other to form three or more systems.

[0029] A first buffer tank 21 for storing the fluorine gas conveyed by the first pump 17 is provided in the first main passage 15 downstream of the first pump 17. The fluorine gas stored in the buffer tank 21 is supplied to the external device 4. A flow meter 26 that detects a flow rate of the fluorine gas supplied to the external device 4 is provided downstream of the first buffer tank 21. A detection result from the flow meter 26 is output to a controller 10c. The controller 10c controls a current value supplied between the anode 7 and the cathode 8 from the power supply 9 on the basis of the detection result from the flow meter 26. More specifically, a fluorine gas amount generated in the anode 7 is controlled such that the first buffer tank 21 is replenished with an amount of fluorine gas corresponding to the amount of fluorine gas supplied to the external device 4 from the first buffer tank 21.

[0030] By controlling the fluorine gas amount generated in the anode 7 so that the fluorine gas supplied to the external device 4 is replaced by an equal amount of fluorine gas in this manner, an internal pressure of the first buffer tank 21 is maintained at a higher pressure than atmospheric pressure. The external device 4 that uses the fluorine gas, on the other hand, is at atmospheric pressure, and therefore, by opening a valve provided in the external device 4, fluorine gas is supplied to the external device 4 from the first buffer tank 21 in accordance with a differential pressure between the first buffer tank 21 and the external device 4.

[0031] A branch passage 22 is connected to the first buffer tank 21, and a pressure regulating valve 23 that controls the internal pressure of the first buffer tank 21 is provided in the branch passage 22. Further, a pressure gauge 24 that detects the internal pressure of the first buffer tank 21 is provided therein. A detection result from the pressure gauge 24 is output to a controller 10d. When the internal pressure of the first buffer tank 21 exceeds a predetermined set value, specifically 1.0MPa, the controller 10d opens the pressure regulating valve 23 to discharge the fluorine gas in the first buffer tank 21. Thus, the pressure regulating valve 23 controls the internal pressure of the first buffer tank 21 so as not to exceed the predetermined pressure.

[0032] A second buffer tank 50 for storing the fluorine gas discharged from the first buffer tank 21 is provided in the branch passage 22 downstream of the pressure regulating valve 23. Hence, when the internal pressure of the first buffer tank 21 exceeds the predetermined pressure, the fluorine gas in the first buffer tank 21 is discharged through the pressure regulating valve 23, and the discharged fluorine gas is led into the second buffer tank 50. The second buffer tank 50 has a smaller capacity than the first buffer tank 21. A pressure regulating valve 51 that controls an internal pressure of the second buffer tank 50 is provided in the branch passage 22 downstream of the second buffer tank 50. Further, a pressure gauge 52 that detects the internal pressure of the second buffer tank 50 is provided therein. A detection result from the pressure gauge 52 is output to a controller 10f. The controller 10f controls an opening of the pressure regulating valve 51 so that the internal pressure of the second buffer tank 50 reaches a predetermined set value. Fluorine gas discharged from the second buffer tank 50 through the pressure regulating valve 51 is discharged after being rendered harmless by a harm removing portion 53. Thus, the pressure regulating valve 51 controls the internal pressure of the second buffer tank 50 to the set value. A fluorine gas supply passage 54 that supplies the fluorine gas to the refining device 16 is connected to the second buffer tank 50.

[0033] Next, the byproduct gas processing system 3 will be described.

[0034] A second main passage 30 for discharging hydrogen gas to the outside is connected to the second gas chamber 12a.

[0035] A second pump 31 that conveys the hydrogen gas from the second gas chamber 12a is provided in the second main passage 30. A second recirculation passage 32 that connects a discharge side and a suction side of the second pump 31 is also connected to the second main passage 30. A second pressure regulating valve 33 for returning hydrogen gas discharged from the second pump 31 to the suction side of the second pump 31 is provided in the second recirculation passage 32.

[0036] An opening of the second pressure regulating valve 33 is controlled by a signal output from the controller 10b. More specifically, the controller 10b controls the opening of the second pressure regulating valve 33 on the basis of the detection result from the second pressure gauge 14 such that the pressure in the second gas chamber 12a reaches a predetermined set value.

[0037] Hence, the pressure in the first gas chamber 11a and the pressure in the second gas chamber 12a are controlled to the predetermined set values by the first pressure regulating valve 19 and the second pressure regulating valve 33, respectively. The set pressures of the first gas chamber 11a and second gas chamber 12a are preferably controlled to equal pressures so that a liquid level difference does not occur between the liquid level of the molten salt in the first gas chamber 11a and the liquid level of the molten salt in the second gas chamber 12a.

[0038] A harm removing portion 34 is provided in the second main passage 30 downstream of the second pump 31, and the hydrogen gas conveyed by the second pump 31 is rendered harmless by the harm removing portion 34 before being discharged.

[0039] The fluorine gas generation device 100 also includes a raw material supply system 5 that supplies the hydrogen fluoride serving as a raw material of the fluorine gas into the molten salt in the electrolytic cell 1. The raw material supply system 5 will now be described.

[0040] A raw material supply passage 41 that leads hydrogen fluoride supplied from a hydrogen fluoride supply source 40 into the molten salt in the electrolytic cell 1 is connected to the electrolytic cell 1. A flow control valve 42 for controlling a supply flow rate of the hydrogen fluoride is provided in the raw material supply passage 41.

[0041] A current integrator 43 that integrates the current supplied between the anode 7 and the cathode 8 is attached to the power supply 9. The current integrated by the current integrator 43 is output to a controller 10e. The controller 10e controls the supply flow rate of the hydrogen fluoride led into the molten salt by opening and closing the flow control valve 42 on the basis of a signal input from the current integrator 43. More specifically, the supply flow rate of the hydrogen fluoride is controlled such that the hydrogen fluoride electrolyzed in the molten salt is replaced. Even more specifically, the supply flow rate of the hydrogen fluoride is controlled such that a hydrogen fluoride concentration of the molten salt remains within a predetermined range.

[0042] A carrier gas supply passage 46 that leads a carrier gas supplied from a carrier gas supply source 45 into the raw material supply passage 41 is connected to the raw material supply passage 41. A shutoff valve 47 that switches between supplying the carrier gas and shutting off the supply is provided in the carrier gas supply passage 46. The carrier gas is a gas for leading the hydrogen fluoride into the molten salt, and nitrogen gas, which is an inert gas, is used here. As a general rule, the shutoff valve 47 is open while the fluorine gas generation device 100 is operative so that the nitrogen gas is supplied into the molten salt in the cathode chamber 12 of the electrolytic cell 1. The nitrogen gas is discharged from the second gas chamber 12a through the byproduct gas processing system 3 substantially without melting into the molten salt.

[0043] When nitrogen gas is supplied into the molten salt in the electrolytic cell 1 in this manner, the molten salt liquid level in the electrolytic cell 1 may be pushed up by the nitrogen gas. To prevent this, a liquid level meter that detects the liquid level may be provided in the electrolytic cell 1, an allowable variation width may be set with respect to the molten salt liquid level of the electrolytic cell 1, and the shutoff valve 47 may be open-close controlled so that the molten salt liquid level remains within the allowable variation width. More specifically, the shutoff valve 47 may be closed when the molten salt liquid level in the electrolytic cell 1 reaches an upper limit of the allowable variation width. It should be noted that a flow control valve capable of controlling a flow rate of the nitrogen gas may be provided instead of the shutoff valve 47.

[0044] Next, overall control of the fluorine gas generation device 100 having the above constitution will be described.

[0045] The flow rate of the fluorine gas used by the external device 4 is detected by the flow meter 26 provided between the first buffer tank 21 and the external device 4. The amount of fluorine gas generated in the anode 7 is controlled by controlling a voltage applied between the anode 7 and the cathode 8 on the basis of the detection result from the flow meter 26. The hydrogen fluoride in the molten salt consumed during the electrolysis is replaced with hydrogen fluoride from the hydrogen fluoride supply source 40.

[0046] By performing control such that the hydrogen fluoride in the molten salt is replenished in accordance with the amount of fluorine gas used by the external device 4 in this manner, the liquid level of the molten salt does not normally vary greatly. However, when the amount of fluorine gas used by the external device 4 varies rapidly or a pressure of the hydrogen gas in the byproduct gas processing system 3 varies rapidly, the pressure in the first gas chamber 11a and the second gas chamber 12a varies greatly, and as a result, the liquid level in the anode chamber 11 and the cathode chamber 12 varies greatly. When the liquid level in the anode chamber 11 and the cathode chamber 12 varies greatly such that the liquid level falls below the partition wall 6, the first gas chamber 11a and the second gas chamber 12a communicate with each other. In this case, the fluorine gas and the hydrogen gas intermix and react.

[0047] To suppress variation in the liquid level in the anode chamber 11 and the cathode chamber 12, the pressure in the first gas chamber 11a and the pressure in the second gas chamber 12a are controlled to the predetermined set value on the basis of the detection results from the first pressure gauge 13 and the second pressure gauge 14, respectively. Hence, the liquid level in the anode chamber 11 and the cathode chamber 12 is controlled by keeping the pressure in the first gas chamber 11a and the second gas chamber 12a constant.

[0048] Next, referring to FIG. 2, the refining device 16 will be described.

[0049] The first refining device 16a and the second refining device 16b are constituted identically, and therefore the following description will focus on the first refining device 16a. Identical constitutions in the second refining device 16b have been allocated identical reference symbols to those of the first refining device 16a, and description thereof has been omitted. Constitutions of the first refining device 16a are differentiated from constitutions of the second refining device 16b by affixing a reference symbol "a" to the former and a reference symbol "b" to the latter.

[0050] The first refining device 16a includes an inner tube 61a serving as a gas inflow portion into which the main product gas containing hydrogen fluoride gas flows, and a cooling device 70a that cools the inner tube 61a to a temperature equal to or higher than a boiling point of fluorine and equal to or lower than a melting point of hydrogen fluoride so that the hydrogen fluoride gas intermixed into the main product gas coagulates but the fluorine gas passes through the inner tube 61a.

[0051] The inner tube 61a is a closed-end tubular member, an upper portion opening of which is sealed by a lid member 62a. An inlet passage 63a that leads the main product gas generated by the anode 7 into the inner tube 61a is connected to the lid member 62a of the inner tube 61a. The inlet passage 63a is constituted by one of two passages obtained by bifurcating the first main passage 15 into two, another inlet passage 63b being connected to an inner tube 61b of the second refining device 16b. An inlet valve 64a that allows the main product gas to flow into the inner tube 61a or blocks the flow is provided in the inlet passage 63a.

[0052] A conduit 67a provided to hang down within the inner tube 61a is coupled to an inner surface of the lid member 62a of the inner tube 61a. A length of the conduit 67a is set such that a lower end opening portion thereof is positioned close to a bottom portion of the inner tube 61a. An upper end portion of the conduit 67a is connected to an outlet passage 65a that is connected to the lid member 62a and discharges fluorine gas from the inner tube 61a. The fluorine gas in the inner tube 61a is therefore discharged to the outside through the conduit 67a and the outlet passage 65a. An outlet valve 66a that allows the fluorine gas to flow out of the inner tube 61a or blocks the flow is provided in the outlet passage 65a. The outlet passage 65a converges with an outlet passage 65b of the second refining device 16b and is thus connected to the first pump 17.

[0053] Hence, the main product gas generated by the anode 7 flows into the inner tube 61a through the inlet passage 63a and flows out of the inner tube 61a through the conduit 67a and the outlet passage 65a.

[0054] When the first refining device 16a is operative, the inlet valve 64a and outlet valve 66a are open, and when the first refining device 16a is stopped or on standby, the inlet valve 64a and outlet valve 66a are closed.

[0055] A thermometer 68a that detects an internal temperature of the inner tube 61a is provided in the inner tube 61a so as to penetrate the lid member 62a. Further, a pressure gauge 69a that detects an internal pressure of the inner tube 61a is provided in the inlet passage 63a.

[0056] The cooling device 70a includes a jacket tube 71a capable of partially accommodating the inner tube 61a and storing liquid nitrogen in its interior as a cooling medium, and a liquid nitrogen supply/ discharge system 72a that supplies and discharges the liquid nitrogen to and from the jacket tube 71a.

[0057] The jacket tube 71a is a closed-end tubular member, an upper portion opening of which is sealed by a lid member 73a. The inner tube 61a is housed coaxially in the jacket tube 71a such that an upper portion side thereof projects from the lid member 73a. More specifically, approximately 80 to 90% of the inner tube 61a is housed in the jacket tube 71a.

[0058] Next, the liquid nitrogen supply/discharge system 72a will be described.

[0059] A liquid nitrogen supply passage 77a that leads liquid nitrogen supplied from a liquid nitrogen supply source 76 into the jacket tube 71a is connected to the lid member 73a of the jacket tube 71a. A conduit 82a provided to hang down within the jacket tube 71a is coupled to an inner surface of the lid member 73a of the jacket tube 71a, and an upper end portion of the conduit 82a is connected to the liquid nitrogen supply passage 77a. Hence, the liquid nitrogen supplied from the liquid nitrogen supply source 76 is led into the jacket tube 71a through the liquid nitrogen supply passage 77a and the conduit 82a. A length of the conduit 82a is set such that a lower end opening portion thereof is positioned close to a bottom portion of the jacket tube 71a.

[0060] A flow control valve 78 for controlling a supply flow rate of the liquid nitrogen is provided in the liquid nitrogen supply passage 77a. A pressure gauge 80a that detects an internal pressure of the jacket tube 71a is provided in the liquid nitrogen supply passage 77a downstream of the flow control valve 78a.

[0061] The interior of the jacket tube 71a is divided into two layers, namely a liquid nitrogen layer and a vaporized nitrogen gas layer, and a liquid level of the liquid nitrogen is detected by a level gauge 74a provided to penetrate the lid member 73a.

[0062] A nitrogen gas discharge passage 79a for discharging the nitrogen gas in the jacket tube 71a is connected to the lid member 73a of the jacket tube 71a. A pressure regulating valve 81a for controlling the internal pressure of the jacket tube 71a is provided in the nitrogen gas discharge passage 79a. The pressure regulating valve 81a controls the internal pressure of the jacket tube 71a to a predetermined pressure on the basis of a detection result from the pressure gauge 80a. The predetermined pressure is determined such that a temperature of the liquid nitrogen in the jacket tube 71a is equal to or higher than the boiling point (-188°C) of fluorine and equal to or lower than the melting point (-84°C) of hydrogen fluoride. More specifically, the predetermined pressure is set at 0.4MPa so that the temperature of the liquid nitrogen in the jacket tube 71a reaches approximately -180°C. Hence, the pressure regulating valve 81a controls the internal pressure of the jacket tube 71a to 0.4MPa so that the temperature of the liquid nitrogen in the jacket tube 71a is maintained at approximately -180°C. The nitrogen gas discharged through the pressure regulating valve 81a is emitted to the outside.

[0063] When the liquid nitrogen in the jacket tube 71a is vaporized and emitted to the outside, the amount of liquid nitrogen in the jacket tube 71a decreases. Accordingly, the flow control valve 78a controls the supply flow rate of the liquid nitrogen from the liquid nitrogen supply source 76 into the jacket tube 71a on the basis of a detection result from the level gauge 74a such that the liquid level of the liquid nitrogen in the jacket tube 71a is kept constant.

[0064] It should be noted that a temperature maintaining insulating material or a vacuum insulation layer may be provided on an outer side of the jacket tube 71a to suppress heat transfer between the jacket tube 71a and the outside.

[0065] The inner tube 61a is cooled to a temperature at equal to or higher than the boiling point of fluorine and at equal to or lower than the melting point of hydrogen fluoride by the jacket tube 71a, and therefore only the hydrogen fluoride gas intermixed into the main product gas coagulates in the inner tube 61a, while the fluorine gas passes through the inner tube 61a. The main product gas is led into the inner tube 61a continuously from the electrolytic cell 1, and therefore the coagulated hydrogen fluoride accumulates in the inner tube 61a over time. When the accumulated amount of coagulated hydrogen fluoride reaches a predetermined amount, an operation changeover is performed on the refining device 16 such that the operation of the first refining device 16a is stopped and the second refining device 16b on standby is activated. This operation changeover will be described in detail below.

[0066] The determination as to whether or not the accumulated amount of coagulated hydrogen fluoride has reached the predetermined amount is made on the basis of a detection result from a differential pressure gauge 86a provided across the inlet passage 63a and the outlet passage 65a, or in other words on the basis of a differential pressure between an inlet and an outlet of the inner tube 61a. When the differential pressure between the inlet and the outlet of the inner tube 61a reaches a predetermined value, it is determined that the accumulated amount of coagulated hydrogen fluoride in the inner tube 61a has reached the predetermined amount, and the first refining device 16a is stopped. The differential pressure gauge 86a corresponds to an accumulation condition detector for detecting an accumulation condition of the hydrogen fluoride in the inner tube 61a. It should be noted that instead of a differential pressure gauge, the accumulation condition of the hydrogen fluoride in the inner tube 61a may be detected using the pressure gauge 69a.

[0067] The first refining device 16a is stopped by closing the inlet valve 64a and the outlet valve 66a of the inner tube 61a. After stopping the first refining device 16a, the first refining device 16a must be set in a standby condition by discharging the coagulated hydrogen fluoride accumulated in the inner tube 61a. In other words, a regeneration process must be performed on the first refining device 16a.

[0068] Next, a system for performing the regeneration process on the first refining device 16a will be described.

[0069] A discharge valve 91a capable of discharging the liquid nitrogen in the jacket tube 71a to an external tank 90a is provided in the bottom portion of the jacket tube 71a. Further, a nitrogen gas supply passage 93a that leads nitrogen gas supplied from a nitrogen gas supply source 92 into the jacket tube 71a is connected to the liquid nitrogen supply passage 77a downstream of the flow control valve 78a. A shutoff valve 94a that switches between supplying nitrogen gas to the jacket tube 71a and shutting off the supply is provided in the nitrogen gas supply passage 93a. Nitrogen gas is supplied to the jacket tube 71a from the nitrogen gas supply source 92 in a condition where the discharge valve 91a is fully open and the flow control valve 78a is fully closed. Gas at room temperature is used as the nitrogen gas.

[0070] Hence, in the jacket tube 71a, room temperature nitrogen gas is supplied while liquid nitrogen is discharged. As a result, the temperature of the inner tube 61a rises, causing the coagulated hydrogen fluoride to dissolve.

[0071] A discharge passage 95a for discharging the dissolved hydrogen fluoride to the outside is connected to the inlet passage 63a downstream of the inlet valve 64a. A discharge pump 96 for suctioning and conveying the dissolved hydrogen fluoride in the jacket tube 71a is provided in the discharge passage 95a, and a discharge valve 97a that opens during discharge of the hydrogen fluoride is provided upstream of the discharge pump 96. Further, a harm removing portion 98 is provided in the discharge passage 95a downstream of the discharge pump 96 so that the hydrogen fluoride conveyed by the discharge pump 96 is rendered harmless by the harm removing portion 98 before being emitted.

[0072] A nitrogen gas supply passage 99a that leads the nitrogen gas supplied from the nitrogen gas supply source 92 into the inner tube 61a is connected to the outlet passage 65a upstream of the outlet valve 66a. A shutoff valve 87a that switches between supplying nitrogen gas to the inner tube 61a and shutting off the supply is provided in the nitrogen gas supply passage 99a. Nitrogen gas is supplied to the inner tube 61a from the nitrogen gas supply source 92 in a condition where the discharge valve 97a is fully open and the discharge pump 96 is activated.

[0073] Hence, in the inner tube 61a, the dissolved hydrogen fluoride is suctioned by the discharge pump 96 while room temperature nitrogen gas is supplied. As a result, the hydrogen fluoride in the inner tube 61a is discharged. The gas in the inner tube 61a is discharged by the discharge pump 96 until the internal pressure of the inner tube 61a, detected by the pressure gauge 69a, falls to or below atmospheric pressure.

[0074] The hydrogen fluoride discharged from the inner tube 61a by the discharge pump 69 may be returned to the hydrogen fluoride supply source 40 for reuse or returned to the electrolytic cell 1 for reuse.

[0075] After discharging the hydrogen fluoride in the inner tube 61a, fluorine gas is charged into the inner tube 61a. This process is performed in order to change back to the first refining device 16a quickly when the second refining device 16b is operative and the accumulated amount of coagulated hydrogen fluoride in the inner tube 61b reaches the predetermined amount.

[0076] Fluorine gas is charged into the inner tube 61a through the fluorine gas supply passage 54 that is connected to the second buffer tank 50 and connected at a downstream end thereof to the inlet passage 63a downstream of the inlet valve 64a. A shutoff valve 88a that opens when fluorine gas is charged into the inner tube 61a is provided in the fluorine gas supply passage 54.

[0077] The internal pressure of the second buffer tank 50 is controlled by the pressure regulating valve 51 to a higher pressure than atmospheric pressure, and therefore the fluorine gas stored in the second buffer tank 50 is supplied into the inner tube 61a by a differential pressure between the second buffer tank 50 and the inner tube 61a. Hence, fluorine gas is charged into the inner tube 61a using the fluorine gas stored in the second buffer tank 50.

[0078] Next, an operation of the refining device 16 having the above constitution will be described. The following operation of the refining device 16 is controlled by a controller (not shown) serving as a control device installed in the fluorine gas generation device 100. The controller controls operations of the respective valves and pumps on the basis of detection results from the thermometer 68a, the pressure gauge 69a, the level gauge 74a, the pressure gauge 80a, and the differential pressure gauge 86a.

[0079] A case in which the first refining device 16a is operative and the second refining device 16b is on standby will be described. In the first refining device 16a, the inlet valve 64a and outlet valve 66a of the inner tube 61a are open, and therefore the main product gas is led into the inner tube 61a from the electrolytic cell 1 continuously. In the second refining device 16b, on the other hand, the inlet valve 64b and outlet valve 66b of the inner tube 61b are closed, and therefore fluorine gas is charged into the inner tube 61b. Hence, the fluorine gas generated by the electrolytic cell 1 is supplied to the refining device 16a alone.

[0080] The operative first refining device 16a will now be described.

[0081] Liquid nitrogen led through the liquid nitrogen supply passage 77a is stored in the jacket tube 71a of the first refining device 16a, and the inner tube 61a is cooled by the liquid nitrogen. The internal pressure of the jacket tube 71a is controlled to 0.4MPa by the pressure regulating valve 81a. Accordingly, the temperature of the liquid nitrogen in the jacket tube 71a is maintained at approximately -180°C, which is higher than the boiling point of fluorine and lower than the melting point of hydrogen fluoride, and therefore only the hydrogen fluoride coagulates in the inner tube 61a, while the fluorine gas is conveyed through the inner tube 61a into the first buffer tank 21 by the first pump 17.

[0082] Here, the main product gas generated by the electrolytic cell 1 flows into the inner tube 61a through the inlet passage 63a and flows out of the inner tube 61a through the conduit 67a and the outlet passage 65a. The lower end opening portion of the conduit 67a is positioned close to the bottom portion of the inner tube 61a, and therefore the main product gas flows in from the upper portion of the inner tube 61a and flows out from the lower portion of the inner tube 61a. Hence, the main product gas is cooled sufficiently while passing through the inner tube 61a, and therefore the hydrogen fluoride gas in the main product gas can be coagulated reliably and removed completely.

[0083] The main product gas is led into the inner tube 61a from the electrolytic cell 1 continuously, and therefore the liquid nitrogen in the jacket tube 71a for cooling the main product gas vaporizes continuously. The resulting vaporized nitrogen gas is emitted to the outside via the pressure regulating valve 81a.

[0084] The accumulated amount of coagulated hydrogen fluoride in the inner tube 61a increases, and when the differential pressure between the inlet and the outlet of the inner tube 61, detected by the differential pressure gauge 86a, reaches the predetermined value, the operation changeover is performed on the refining device 16 such that the operation of the first refining device 16a is stopped and the second refining device 16b on standby is activated. After stopping the operation of the first refining device 16a, the regeneration process is performed thereon.

[0085] Next, referring also to FIG. 3, the operation changeover from the first refining device 16a to the second refining device 16b and the regeneration process performed on the first refining device 16a will be described. FIG. 3 is a graph showing temporal variation in the pressure and temperature in the inner tube 61a of the first refining device 16a, on which a solid line indicates the pressure and a dot-dash line indicates the temperature. The pressure shown in FIG. 3 is the pressure detected by the pressure gauge 69a, and the temperature is the temperature detected by the thermometer 68a.

[0086] As shown in FIG. 3, as the accumulated amount of coagulated hydrogen fluoride in the inner tube 61a increases, the internal pressure of the inner tube 61a rises. When the internal pressure of the inner tube 61a reaches a predetermined pressure (Ph) such that the differential pressure between the inlet and the outlet of the inner tube 61a, detected by the differential pressure gauge 86a, reaches the predetermined value, the operation changeover from the first refining device 16a to the second refining device 16b is performed (time t1). More specifically, the inlet valve 64b and outlet valve 66b of the inner tube 61b in the second refining device 16b are opened, whereupon the inlet valve 64a and outlet valve 66a of the inner tube 61a in the first refining device 16a are closed. As a result, the second refining device 16b is activated and the first refining device 16a is stopped such that the main product gas from the electrolytic cell 1 is led into the second refining device 16b.

[0087] In the stopped first refining device 16a, the liquid nitrogen in the jacket tube 71a is discharged. More specifically, the flow control valve 78a of the liquid nitrogen supply passage 77a is fully closed to stop the supply of liquid nitrogen into the jacket tube 71a, whereupon the discharge valve 91a is fully opened such that the liquid nitrogen is discharged. The shutoff valve 94a in the nitrogen gas supply passage 93a is then opened such that room temperature nitrogen gas is supplied into the jacket tube 71a. As a result, as shown in FIG. 3, the internal temperature of the inner tube 61a rises to approximately room temperature, whereby the hydrogen fluoride in the inner tube 61a dissolves.

[0088] As the internal temperature of the inner tube 61a rises, the discharge valve 97a in the discharge passage 95a is opened, thereby activating the discharge pump 96. As a result, the dissolved hydrogen fluoride in the inner tube 61a is suctioned by the discharge pump 96 and conveyed to the harm removing portion 98. At the same time, the shutoff valve 87a in the nitrogen gas supply passage 99a is opened such that room temperature nitrogen gas is supplied into the inner tube 61a. Hence, in the inner tube 61a, the dissolved hydrogen fluoride is discharged while room temperature nitrogen gas is supplied. When the internal pressure of the inner tube 61a falls to a predetermined pressure (P1) at or below atmospheric pressure (time t2), it is determined that discharge of the hydrogen fluoride in the inner tube 61a is complete, and therefore the discharge valve 97a in the discharge passage 95a and the shutoff valve 87a in the nitrogen gas supply passage 99a are fully closed. At this point, discharge of the hydrogen fluoride in the inner tube 61a is complete.

[0089] When discharge of the hydrogen fluoride in the inner tube 61a is completed, liquid nitrogen is supplied into the jacket tube 71a and fluorine gas is supplied into the inner tube 61a in order to set the first refining device 16a in a standby condition. More specifically, with the discharge valve 91a and the shutoff valve 94a of the nitrogen gas supply passage 93a fully closed, the flow control valve 78a in the liquid nitrogen supply passage 77a is reopened so that liquid nitrogen is supplied into the jacket tube 71a (time t3). Accordingly, the internal temperature of the inner tube 61a decreases. The internal pressure of the jacket tube 71a is controlled to 0.4MPa by the pressure regulating valve 81a, and therefore the internal temperature of the inner tube 61a is reduced to and maintained at approximately -180°C. Further, as the internal temperature of the inner tube 61a decreases, the shutoff valve 88a in the fluorine gas supply passage 54 is opened such that fluorine gas is supplied into the inner tube 61a from the second buffer tank 50 (time t4). As the fluorine gas is supplied into the inner tube 61a, the internal pressure of the inner tube 61a increases, and when the internal pressure reaches atmospheric pressure, the shutoff valve 88a is closed to stop the supply of fluorine gas. Fluorine gas is thus charged into the inner tube 61a. At this point, the regeneration process of the first refining device 16a is complete, and therefore the first refining device enters standby (time t5).

[0090] Hence, the fluorine gas in the second buffer tank 50 is used as the fluorine gas supplied into the inner tube 61a during the regeneration process. The second buffer tank 50 is used to store the fluorine gas that is discharged during control of the internal pressure of the first buffer tank 21. In other words, fluorine gas that is conventionally emitted to the outside from the first buffer tank 21 is stored in the second buffer tank 50 and used during the regeneration process. Therefore, gas that is conventionally emitted to the outside is used as the fluorine gas supplied into the inner tube 61a in the regeneration process.

[0091] As described above, the stopped first refining device 16a is set in the standby condition by cooling the inner tube 61a to -180°C and charging fluorine gas into the inner tube 61a. Therefore, when the differential pressure between the inlet and the outlet of the inner tube 61b in the operative second refining device 16b reaches the predetermined value, the operation changeover can be performed on the refining device 16 by stopping the operation of the second refining device 16b and quickly activating the first refining device 16a.

[0092] Following actions and effects can be obtained with the embodiment described above.

[0093] At least two of the refining devices 16 are disposed parallel to each other, and the refining device 16 of the system that is stopped by the operation changeover is set in the standby condition by discharging the hydrogen fluoride from the inner tube 61 and then supplying fluorine gas to the inner tube 61. Thus the refining device 16 on standby can be operated at any time. Therefore, the refining device 16 of the system on standby can be activated quickly even when the accumulated amount of coagulated hydrogen fluoride in the refining device 16 of the operative system is large such that the refining device 16 must be stopped. Accordingly, the fluorine gas generation device 100 itself need not be stopped, and therefore fluorine gas can be supplied to the external device 4 with stability.

[0094] Further, fluorine gas that is conventionally emitted to the outside is used as the fluorine gas supplied into the inner tube 61 during the regeneration process of the refining device 16, and therefore the fluorine gas can be used effectively. Furthermore, by using fluorine gas that is conventionally emitted to the outside in the regeneration process, the amount of fluorine gas emitted to the outside can be reduced, leading to a reduction in the amount of fluorine gas treated by the harm removing portion 53, and as a result, a load on the harm removing portion 53 can be reduced.

[0095] Other embodiments of this invention are described below.

[0096] In the above embodiment, gas stored in the second buffer tank 50 is used as the fluorine gas employed in the regeneration process, but the fluorine gas stored in the first buffer tank 21 may be used as the fluorine gas employed in the regeneration process instead. In this case, the fluorine gas supply passage 54 is connected to the first buffer tank 21. In this case, however, the pressure in the first buffer tank 21 varies easily, and therefore the pressure of the fluorine gas supplied to the external device 4 may vary. Hence, as described in the above embodiment, the fluorine gas stored in the second buffer tank 50 is preferably used as the fluorine gas employed in the regeneration process.

[0097] This invention is not limited to the embodiments described above and may of course be subjected to various modifications within the scope of the technical idea thereof.

[0098] With respect to the above description, the contents of Japanese patent application No. 2009-89444, with a filing date of April 1, 2009, are incorporated herein by reference.

INDUSTRIAL APPLICABILITY

[0099] This invention may be applied to a device that generates fluorine gas.

Claims

1. A fluorine gas generation device that generates fluorine gas by electrolyzing hydrogen fluoride in molten salt, comprising:

    an electrolytic cell storing the molten salt, in which a first gas chamber to which a main product gas having fluorine gas generated by an anode submerged in the molten salt as a main component is led and a second gas chamber to which a byproduct gas having hydrogen gas generated by a cathode submerged in the molten salt as a main component is led are separated and defined above a liquid level of the molten salt;
    a refining device that refines the fluorine gas by scavenging hydrogen fluoride gas that is vaporized from the molten salt in the electrolytic cell and intermixed into the main product gas generated by the anode; and
    a control device that controls an operation of the refining device,
    wherein at least two of the refining devices are disposed parallel to each other, each refining device comprising:

        a gas inflow portion into which the main product gas containing the hydrogen fluoride gas flows;
        a cooling device that cools the gas inflow portion to a temperature equal to or higher than a boiling point of fluorine and equal to or lower than a melting point of hydrogen fluoride such that the hydrogen fluoride gas intermixed into the main product gas coagulates while the fluorine gas passes through the gas inflow portion; and
        an accumulation condition detector that detects an accumulation condition of the hydrogen fluoride in the gas inflow portion, and the control device performs an operation changeover on the refining device on the basis of a detection result from the accumulation condition detector so that fluorine gas is led into a refining device on standby, and sets a refining device stopped by the operation changeover in a standby condition by discharging the hydrogen fluoride from the gas inflow portion of the stopped refining device and supplying fluorine gas to the gas inflow portion thereof.

2. The fluorine gas generation device as defined in Claim 1, comprising:

    a first main passage connected to the first gas chamber in order to supply the fluorine gas generated by the anode of the electrolytic cell to an external device;
    a first buffer tank provided in the first main passage in order to store the fluorine gas;
    a branch passage connected to the first buffer tank;
    a pressure regulating valve provided in the branch passage in order to control an internal pressure of the first buffer tank; and
    a second buffer tank for storing fluorine gas discharged from the first buffer tank through the pressure regulating valve,
    wherein, when the stopped refining device is set in the standby condition, the fluorine gas stored in the first buffer tank or the second buffer tank is supplied to the gas inflow portion.

3. The fluorine gas generation device as defined in Claim 1, wherein the hydrogen fluoride discharged from the gas inflow portion during the operation changeover is returned to the electrolytic cell.

4. The fluorine gas generation device as defined in Claim 1, further comprising a hydrogen fluoride supply source storing hydrogen fluoride for replenishing the electrolytic cell,
    wherein the hydrogen fluoride discharged from the gas inflow portion during the operation changeover is returned to the hydrogen fluoride supply source.

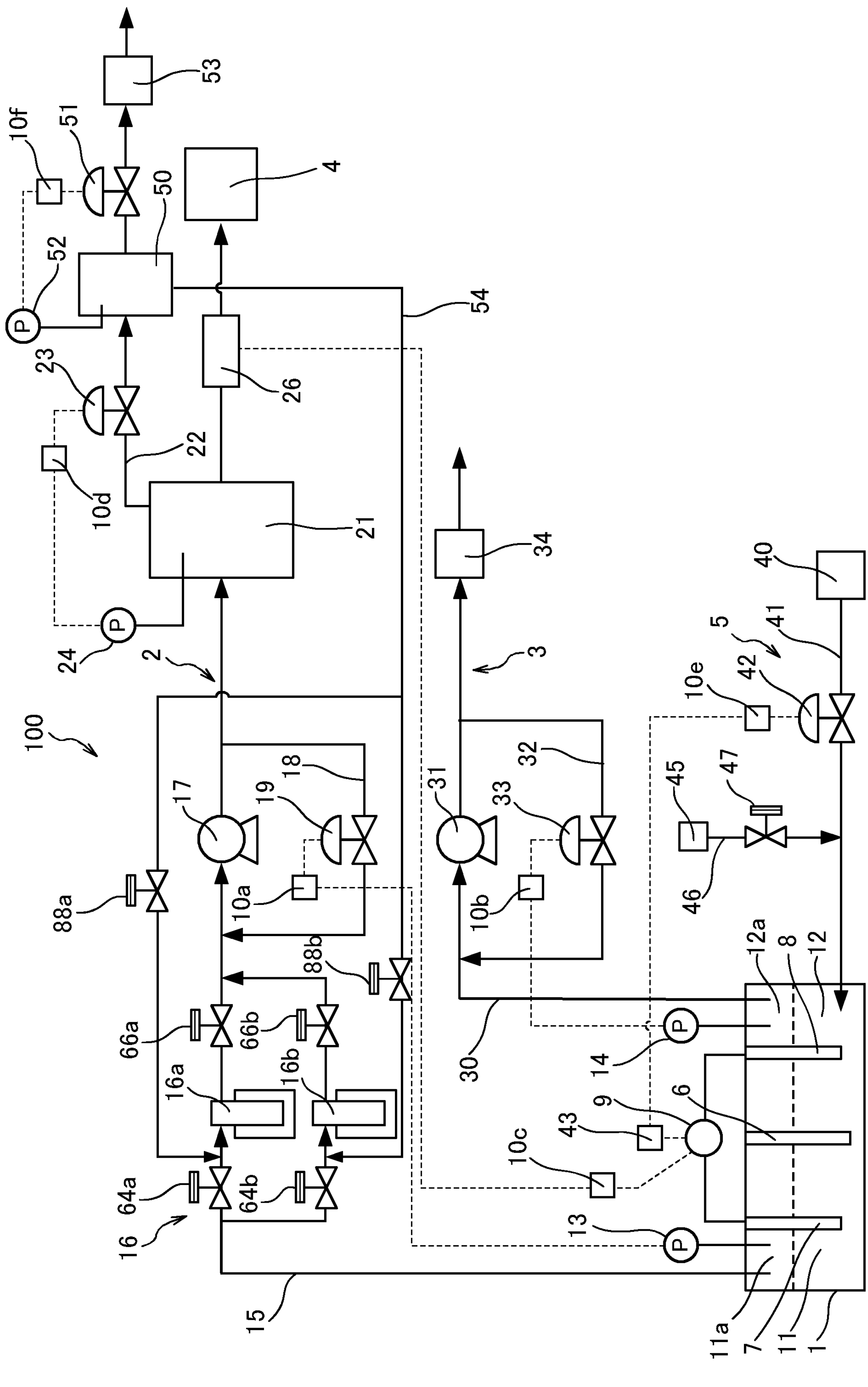
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FIG. 1

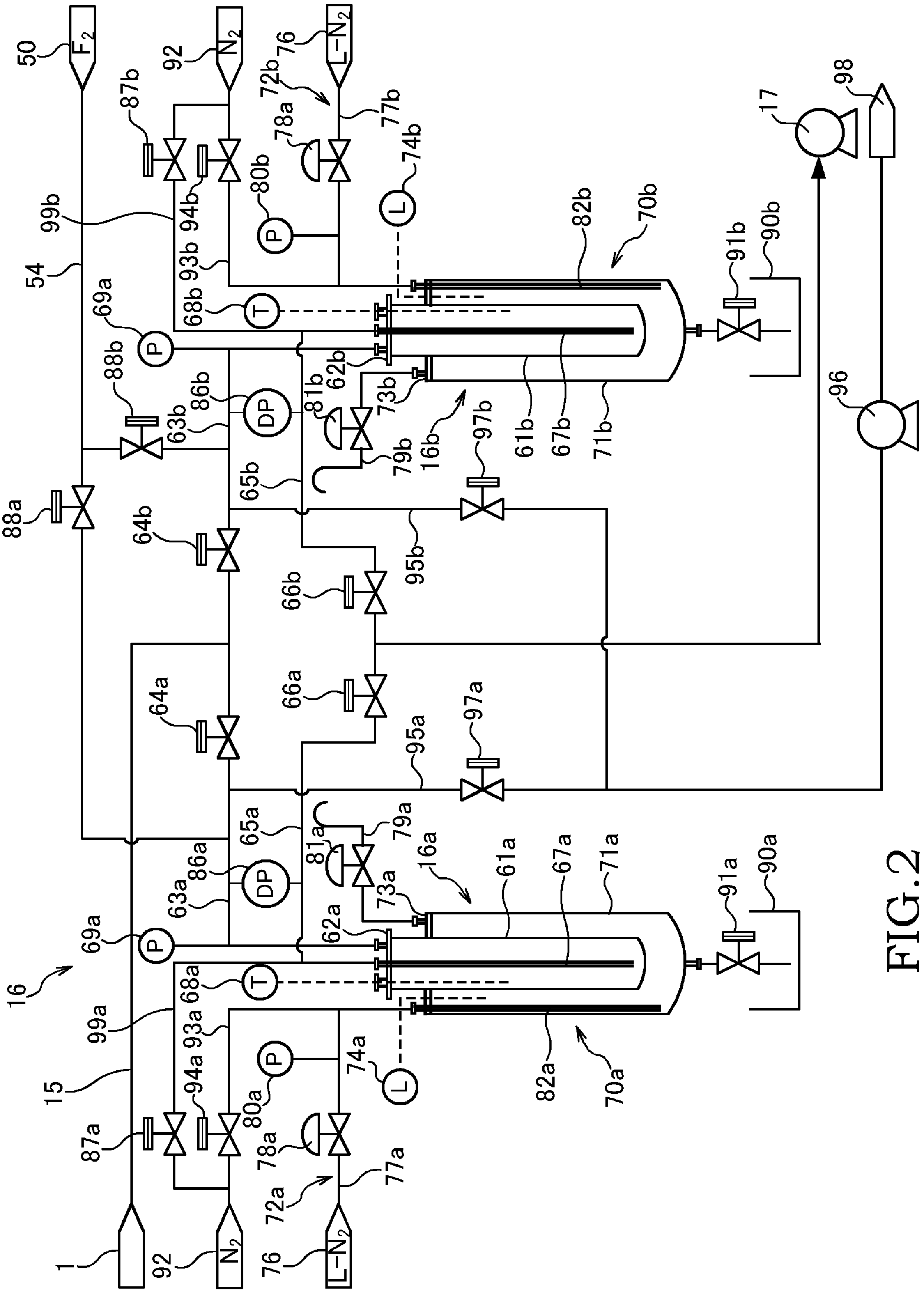
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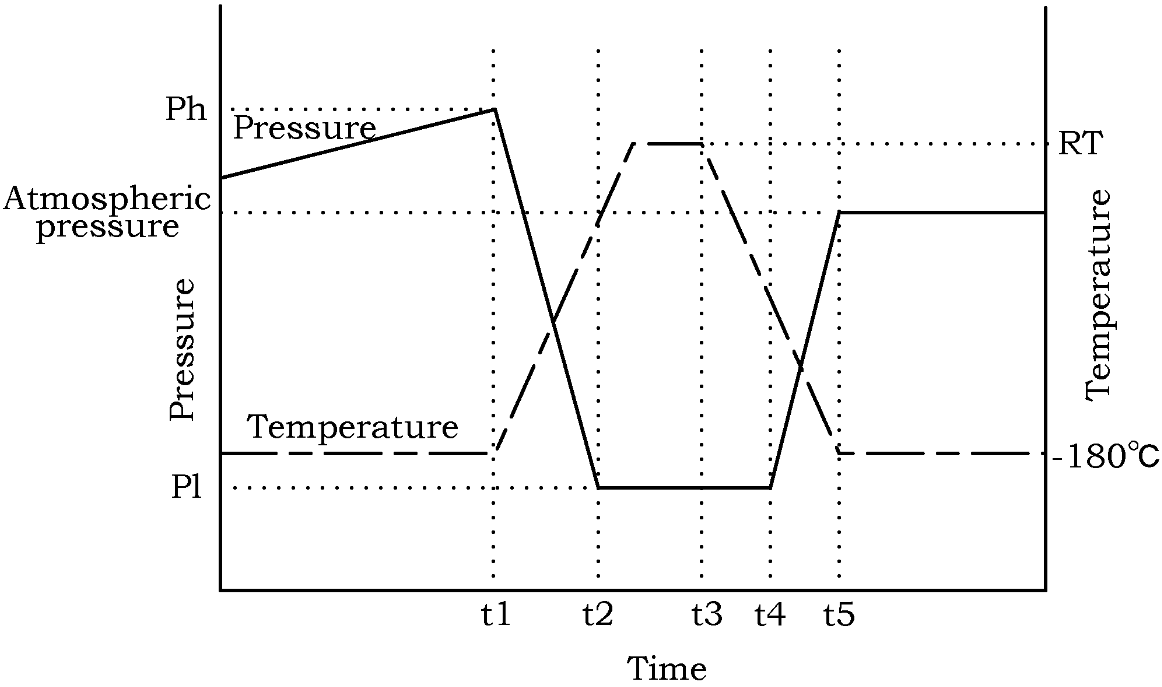
FIG.2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t3
t4
t5
Time

FIG.3

INTERNATIONAL SEARCH REPORT

International application No. PCT/JP2010/054061

A. CLASSIFICATION OF SUBJECT MATTER
C25B1/24(2006.01)i, *C25B9/00*(2006.01)i, *C25B15/08*(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C25B1/24, C25B9/00, C25B15/08, C01B7/20

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Jitsuyo Shinan Koho	1922-1996	Jitsuyo Shinan Toroku Koho	1996-2010
Kokai Jitsuyo Shinan Koho	1971-2010	Toroku Jitsuyo Shinan Koho	1994-2010

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2005-264231 A (L'Air Liguide, Societe Anonyme a Directoire et Conceil de Surveillance pour l'Etude et l'Exploitation des Procedes Georges Claude), 29 September 2005 (29.09.2005), entire text (Family: none)	1-4
A	JP 2004-39740 A (Research Institute Of Innovative Technology For The Earth, National Institute Of Advanced Industrial Science And Technology), 05 February 2004 (05.02.2004), entire text & US 2005/0252451 A1 & EP 1542264 A1 & WO 2004/003983 A1 & TW 583334 B & CN 1565046 A	1-4

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

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"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
06 April, 2010 (06.04.10)	20 April, 2010 (20.04.10)
Name and mailing address of the ISA/ Japanese Patent Office	Authorized officer
Facsimile No.	Telephone No.

Form PCT/ISA/210 (second sheet) (July 2009)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2010/054061

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2006-501118 A (Fluorine On Call, Ltd.), 12 January 2006 (12.01.2006), entire text & US 2004/0037768 A1 & US 2003/0098038 A1 & US 2003/0121796 A1 & US 2004/0151656 A1 & US 2009/0001524 A1 & EP 1455918 A & WO 2003/046244 A2 & CN 1610573 A & KR 10-2009-0086284 A	1-4

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REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- JP 2004043885 A **[0003]**
- JP 2004039740 A **[0005] [0006]**
- JP 2009089444 A **[0098]**