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(54) Method of nitriding nickel alloy.

(57) A method of nitriding nickel alloy comprising heating nickel alloy in an atmosphere of fluorine- or fluoride-containing gas to fluorinate the nickel alloy and heating the fluorinated nickel alloy in a nitriding atmosphere. The nitrided nickel alloy has an improved surface hardness with a deep uniform nitrided layer on its surface.

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This invention relates to a method for nitriding nickel alloy for the improvement of surface hardness and other properties by forming a nitrided layer on nickel alloy surface.

Alloy with a high nickel content, such as inconel(Ni-Cr), hastelloy(Ni-Cr-Mo) and incolloy,has been becoming widely employed because of its superior heat resistance and corrosion resistance. Recently there is an increasing demand for improving wear resistance and other properties of alloy containing nickel and expanding its applicable fields. However, for the above-mentioned nickel alloy such as inconel, the method for the improvement of surface hardness has not been established yet. A method of push-out hardening for the improvement of base material intensity and a use of superplastic articles employing powder material are merely studied. However, since the method of push-out hardening increases stiffness of whole alloy, workability of the alloy is damaged. Also superplastic articles employing powder material are difficult to put into practical use due to extremely high cost.

Conventional methods of surface hardening for general metallic materials are as follows, ① a plating method, ② a coating method such as PVD, and ③ a diffusion method such as nitriding and boriding. However, for nickel alloy, only some of the coating methods, such as full hard chrome plating and alumina coating, find practical use as mentioned above. Those methods have difficulty in quality control which is peculiar to the coating method, and limit the application range due to the thinness of the coating. Moreover, high cost for treatment is another problem. For the diffusion method of surface hardening, plasma ion nitriding using glow discharge has been also tried partly for inconel alloy and hastelloy alloy. However, the treatment of such plasma ion nitriding scarcely forms a hardened nitrided layer on the above-mentioned nickel alloy. Even if formed, that would be a partly formed ultra thin layer only several microns deep. Therefore, in the present situation, nitriding the above-mentioned nickel alloy is almost given up and far from turning it to practical use.

The present invention can provide a method of nitriding nickel alloy for the improvement of the surface hardness of nickel alloy by which a uniformly nitrided deep layer can be formed on the nickel alloy surface.

The present invention provides a method for nitriding nickel alloy which comprises steps of holding nickel alloy in a fluorine- or fluoride-containing gas atmosphere with heating and holding the fluorinated nickel alloy in a nitriding atmosphere with heating to form the surface layer of the nickel alloy into a nitrided layer.

The method of the invention is applied to a nickel alloy, which is nitrided in a nitriding atmosphere after having been flourided in a fluorine- or fluoride-containing gas atmosphere.

Nickel alloys containing more than 25 weight % (it will be abbreviated to " % " hereafter) nickel, for example, Ni-Cr, Ni-Cr-Mo, and Ni-Cr-Fe are mainly used in the method of the invention.

Examples of such alloys with a high nickel content are inconel, hastelloy, and incolloy. Nickel alloys containing not more than 25% nickel can be also used in the method of the invention. Therefore, in the invention, the term " nickel alloy" includes both alloys containing more than 25% nickel and not more than 25% nickel. However, alloy containing more than 25% nickel is more suitable. A method does not specify a shape of nickel alloy nor a level of processing. All the material, intermediate products, and finished products made of nickel alloy are included to the extent of nickel alloy in this invention.

, Fluorine- or fluoride-containing gas for a fluorine- or fluoride-containing gas atmosphere, in which the above-mentioned nickel alloy is reacted, is fluorine compound gas, such as NF_3, BF_3, CF_4, HF, SF_6, C_2F_6, WF_6, CHF_3, or SiF_4. They are used independently or in combination. Besides, fluorine compound gas with F in its molecule can be used as the above-mentioned fluorine- or fluoride-containing gas. Also F_2 gas formed by cracking fluorine compound gas in a heat decomposition device and preliminarily formed F_2 gas are employed as the above-mentioned fluorine- or fluoride-containing gas. According to the case, such fluorine compound gas and F_2 gas are mixed for use. The above-mentioned fluorine or fluoride-containing gas such as the fluorine compound gas and F_2 gas can be used independently, but generally are diluted by inert gas such as N_2 gas for the treatment. The concentration of the fluorine- or fluoride-containing gas itself in such diluted gas should amount to , for example, 10,000 to 100,000ppm, preferably 20,000 to 70,000ppm, more preferably 30,000 to 50,000ppm.

In the invention, the above-mentioned nickel alloy is held in a heated condition in a fluorine- or fluoride-containing gas atmosphere of such concentration, and fluorided. This is the most characteristic part of the invention. In this case, nickel alloy is held with heating at a temperature of, for example, 350 to 500 °C. The holding time of the above-mentioned nickel alloy in a fluorine- or fluoride-containing gas atmosphere may appropriately be selected depending on the nickel alloy species, geometry and dimension of the alloy, heating temperature and the like, generally within the range of about ten minutes to several hours. 30 minutes is a preferred exposure time. The treatment of nickel alloy in such fluorine- or fluoride-containing gas atmosphere allows "N" atoms to penetrate into nickel alloy, which was impossible in the past.

Though the mechanism of the penetration has not yet been proven , it can be largely understood as follows.

The oxidized layer of NiO formed on the nickel alloy surface inhibits penetration of "N" atoms for nitrization. Upon holding nickel alloy with an oxidized layer in a fluorine- or fluoride-containing gas atmosphere with heating as mentioned above, the oxidized layer of NiO is converted to a fluorinated layer of NiF_2. "N" atoms for nitrization penetrate more readily into the fluorinated layer of NiF_2 than into the oxidized layer of NiO, that is, a nickel alloy surface is formed which is in a suitable condition for the penetration of "N" atoms by the above-mentioned fluorination. Thus, it is considered that "N" atoms in the nitriding gas penetrate uniformly into nickel alloy to a certain depth when nickel alloy is held in a nitriding atmosphere with such a suitable surface condition to absorb "N" atoms as follows, resulting the formation of a deep uniform nitriding layer.

Then, as mentioned above, nickel alloy with suitable surface condition to absorb "N" atoms by fluorination is held with heating in a nitriding atmosphere to nitride. In this case, nitriding gas composing a nitriding atmosphere is a simple gas composed of NH_3 only, or a mixed gas composed of NH_3 and a carbon source gas, for example, RX gas. Mixture of both gases can be also used. Generally, the above-mentioned simple gas mixed with an inert gas such as N_2 is used. According to the case, H_2 gas is added to those gases.

In such a nitriding atmosphere, the above-mentioned fluorinated nickel alloy is held with heating. A heating condition is generally set at a temperature of 500 to 700 °C, and treatment time is set within the range of 3 to 6 hours. By this nitriding treatment, a close nitriding layer (consisting of entirely single layer) is formed deeply and uniformly on the surface of the above-mentioned nickel alloy, whereby the surface hardness of nickel alloy reaches Hv = 800 to 1100 in comparison with that of base material thereof Hv = 280 to 380. Thickness of the hardened layer basically depends on the nitriding temperature and time. However the temperature below 500 °C causes difficulty in forming a nitriding layer, and at the temperature over 650 °C, a fluorinated layer is damaged and Ni is easily oxidized thereby resulting in a tendency of unevenly nitrided layer formation.

On the other hand, a sufficient fluorinated layer ordinarily can not be formed at the fluoriding temperature below 400 °C. Also the temperature over 600 °C is not appropriate for an industrial process because furnace materials in a muffle furnace are worn out due to extreme fluoriding reaction. From a viewpoint of forming a nitriding layer, it is also preferable that the difference between fluoriding temperature and nitriding temperature is as small as possible. For example, a proper nitriding layer is not formed by nitriding given after fluoriding and cooling once.

The above-mentioned fluoriding and nitriding steps are, for example, taken in a metallic muffle furnace as shown in Fig. 1, that is, the fluoriding treatment is carried out first, and then nitriding treatment is put in practice at the inside of the muffle furnace. In Fig. 1, the reference numeral 1 is a muffle furnace, 2 an outer shell of the muffle furnace, 3 a heater, 4 an inner vessel, 5 a gas inlet pipe, 6 an exhaust pipe, 7 a motor, 8 a fan, 11 a metallic container, 13 a vacuum pump, 14 a noxious substance eliminator, 15 and 16 cylinders, 17 flow meters, and 18 a valve. Nickel alloy articles 10 are put in the furnace 1 and fluorided by introducing fluorine- or fluoride-containing gas atmosphere such as NF_3 with heating. The gas is lead into the exhaust pipe 6 by the action of vacuum pump 13 and detoxicated in the noxious substance eliminator 14 before being spouted out. And then, the cylinder 15 is connected with a duct to carry out nitriding by introducing nitriding gas into the furnace 1. After nitriding, the gas is spouted out via the exhaust pipe 6 and the noxious substance eliminator 14. Through the series of these operations, fluoriding and nitriding treatments are put in practice. Also a device in Fig. 2 can be employed instead of one in Fig. 1. This device comprises a fluoriding chamber on the left side and a nitriding chamber on the right side. In the figure, the reference numeral 2' are metallic containers, 3' a heater, 5' an exhaust gas pipe, 6' and 7' open-close covers, 11' a base, 21 a furnace body with adiabatic walls, and 22 a barrier movable up and down. The barrier 22 divides the inner space of the furnace body 21 into two chambers, 23 and 24. The chamber 23 is designed for a fluoriding chamber and 24 is for a nitriding chamber. The reference numeral 25 is a rack comprising two rails on which a metallic container 2' having nickel alloy articles therein can slide back and forth between chamber 23 and 24. The reference numeral 10' is legs of the rack 25. The reference numeral 26 is a gas introducing pipe which leads a fluorine- or fluoride-containing gas into the fluoriding chamber23, 27 a temperature sensor, and 28 a nitriding gas introducing pipe. High-nickel based heat resistance alloy is desirable as material for the above-mentioned metallic muffle furnace 1 instead of stainless steel material.

This device is a continuous treatment system in which the inner temperature of a fluoriding chamber 23 is raised by the heating on nitriding in the nitriding chamber 24, nickel alloy articles are introduced into the fluoriding chamber 23 under that condition to be fluorided. After exhausting the gas in fluoriding chamber 23, the nickel alloy articles together with the metallic container are transferred to the nitriding chamber 24 by opening and shutting the barrier 22. And then, nitriding is carried out under that condition thereby conducting fluoriding and nitriding continuously.

The adoption of NF_3 as fluorine- or fluoride-containing gas is suitable in particular for the above-mentioned fluoriding. That is, NF_3 is a handy gaseous substance that has no reactivity at the ordinary temperature allowing operations and detoxication of exhaust gas to be easy.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 schematically shows a construction of a treatment furnace for carrying out nitriding according to the invention,
Fig. 2 schematically shows a construction of another furnace, for carrying out nitriding according to the invention,
Fig. 3 is an enlarged sectional view of a nitrided nickel alloy plate (inconel 600),
Fig. 4 is an enlarged sectional view of a nitrided nickel alloy plate (inconel 751), and
Fig. 5 is an enlarged sectional view of a nitrided nickel alloy plate (hastelloy C).

The following modes for carrying out the invention illustrate the invention.

Example 1

Three kinds of nickel alloy plates made of inconel 600 (Ni:76, Cr:16, Fe:8), inconel 751 (Ni:73, Cr:16, Ti:2.5), and hastelloy C (Ni:56, Cr:16, Mo:7) were charged into a treatment furnace as shown in Fig. 1. After vacuum purging the inside of the furnace, it was heated to 550 °C. Then, in that state, fluorine- or fluoride-containing gas (NF_3 10 Vo1% + N_2 90 Vo1%) was charged into the furnace to form an atmospheric pressure in it and the condition was maintained for 30 minutes. Then after exhausting the above-mentioned fluorine- or fluoride-containing gas out of the furnace, nitriding gas (NH_3 50 Vo1% + N_2 25 Vo1% + H_2 25 Vo1%) was introduced into the furnace and the inside of the furnace was heated to 570 °C. Nitriding treatment was carried out in this condition for 3 hours. Through this nitriding process, surface hardening layers B of a nitrided layer were formed on the surface of three kinds of Nickel alloy plates made of inconel 600, inconel 751, and hastelloy C respectively, and their thickness each was 15 μm, 12 μm, and 10 μm as shown in Fig. 3, Fig. 4, and Fig. 5. In these drawings, "A" shows base material of nickel alloy. Also surface hardness of those surface hardening layers B was Hv = 800~1,000 in each case.

Example 2

Three kinds of nickel alloy plates made of inconel 600, inconel 751, and hastelloy C were charged into a treatment furnace as shown in Fig. 1. After vacuum purging the inside of the furnace, it was heated to 350 °C. Then, in that state, fluorine- or fluoride-containing gas (NF_3 10 Vo1% + N_2 90 Vo1%) was charged into the furnace to form an atmospheric pressure in it and the condition was maintained for 30 minutes. Then after exhausting the above-mentioned fluorine- or fluoride-containing gas out of the furnace, nitriding gas (NH_3 50 Vo1% + RX 50 vo1%) was introduced into the furnace and the inside of the furnace was heated to 530 °C. Nitriding treatment was carried out in this condition for 5 hours. Through this nitriding process, surface hardening layers of a nitrided layer were formed on the surface of three kinds of nickel alloy plates made of inconel 600, inconel 751, and hastelloy C respectively, and their thickness each was 12 μm, 12 μm, and 10 μm. Also surface hardness of those surface hardening layers was Hv = 650~1,050 in each case.

Example 3

As to three kinds of nickel alloy plates made of inconel 600, inconel 751, and hastelloy C respectively, fluoriding treatment was carried out in the same way as Example 1. Then nitriding treatment was carried out at the temperature of 620 °C for 3 hours to them while a mixed gas composed of NH_3 50 Vo1% + N_2 50 Vo1% was introduced into the furnaces as a nitriding gas. After nitriding them, fluoriding was carried out at the temperature of 620 °C for 3 hours employing similar fluorine- or fluoride-containing gas mentioned to that of Example 1 and further nitriding treatment was carried out again at the temperature of 620 °C for 3 hours employing the above-mentioned nitriding gas. In this way fluoriding and nitriding were put in practice two times each to three kinds of nickel alloy and thickness of the hard layers made of a nitrided layer formed on those surfaces was measured. As a result, the thickness of each hard layer of inconel 600, inconel 751, and hastelloy C was 25 μm, 20 μm, and 18 μm. It was found their surface hardness was the same as that of Example 1.

Example 4

A mixed gas composed of F_2 10 Vo1% + N_2 90 Vo1% was employed as fluorine- or fluoride-containing gas. Except this difference, all the same fluoriding and nitriding treatments were carried out to three kinds of nickel alloy plates as Example 1. As a result, the same nitrided hard layers as Example 1 were formed on the surface of three kinds of plates after the treatments, and surface hardness was the same as that of Example 1.

As mentioned hereinbefore, the method of nitriding nickel alloy according to the invention comprises holding nickel alloy with heating in a fluorine- or fluoride-containing gas atmosphere to thereby eliminate organic and inorganic contaminants stuck to nickel alloy and at the same time causing an oxidised layer on the nickel alloy surface to be converted to a fluorinated layer, and then subjecting the alloy to the nitriding treatment. Since the oxidised layer on the nickel alloy surface is converted to a fluorinated layer in that manner, an existence of the fluorinated layer protects the nickel alloy surface. Therefore, even after a lapse of certain time from fluoriding to nitriding, the above-mentioned fluorinated layer protects the nickel alloy surface. As a result, no oxidized layer can be formed again on the nickel alloy surface. Since such a fluorinated layer can transmit "N" atoms, "N" atoms can penetrate uniformly into the nickel alloy surface layer to a certain depth at the time of nitriding. The resulting uniform penetration can leads the formation of a close uniform nitriding layer in the depth only in the nickel alloy surface layer and the surface hardness is drastically improved without raising the base material stiffness of the nickel alloy.

Claims

1. A method for nitriding nickel alloy comprising heating nickel alloy in a fluorine- or fluoride-containing gas atmosphere to fluorinate the nickel alloy and heating the fluorinated nickel alloy in a nitriding atmosphere to form a nitrided layer in the surface layer of the nickel alloy.

2. A method for nitriding nickel alloy according to claim 1 in which the fluorine- or fluoride-containing gas atmosphere is composed of at least one of:

(a) a fluorine compound gas containing at least one component selected from the group; NF_3, BF_3, CF_4, HF, SF_6, C_2F_6, WF_6, CHF_3, and SiF_4;

(b) F_2 gas formed by cracking the above-mentioned fluorine compound gas (a); and

(c) pre-formed F_2 gas;

optionally together with an inert gas.

3. A method for nitriding nickel alloy according to claim 1 or 2 in which the nickel alloy is heated in a fluorine- or fluoride-containing gas atmosphere at a temperature between 350 °C and 600 °C.

4. A method for nitriding nickel alloy according to any preceding claim in which the nitriding atmosphere is NH_3 gas a mixture of NH_3 gas and RX gas, an inert gas mixture of an inert gas and NH_3 gas or NH_3 gas RX gas mixture, or a gas mixture formed by mixing H_2 gas with the inert gas mixture.

5. A method for nitriding nickel alloy according to any preceding claim in which the nickel alloy is heated in a nitriding atmosphere at a temperature between 500 °C and 700 °C.

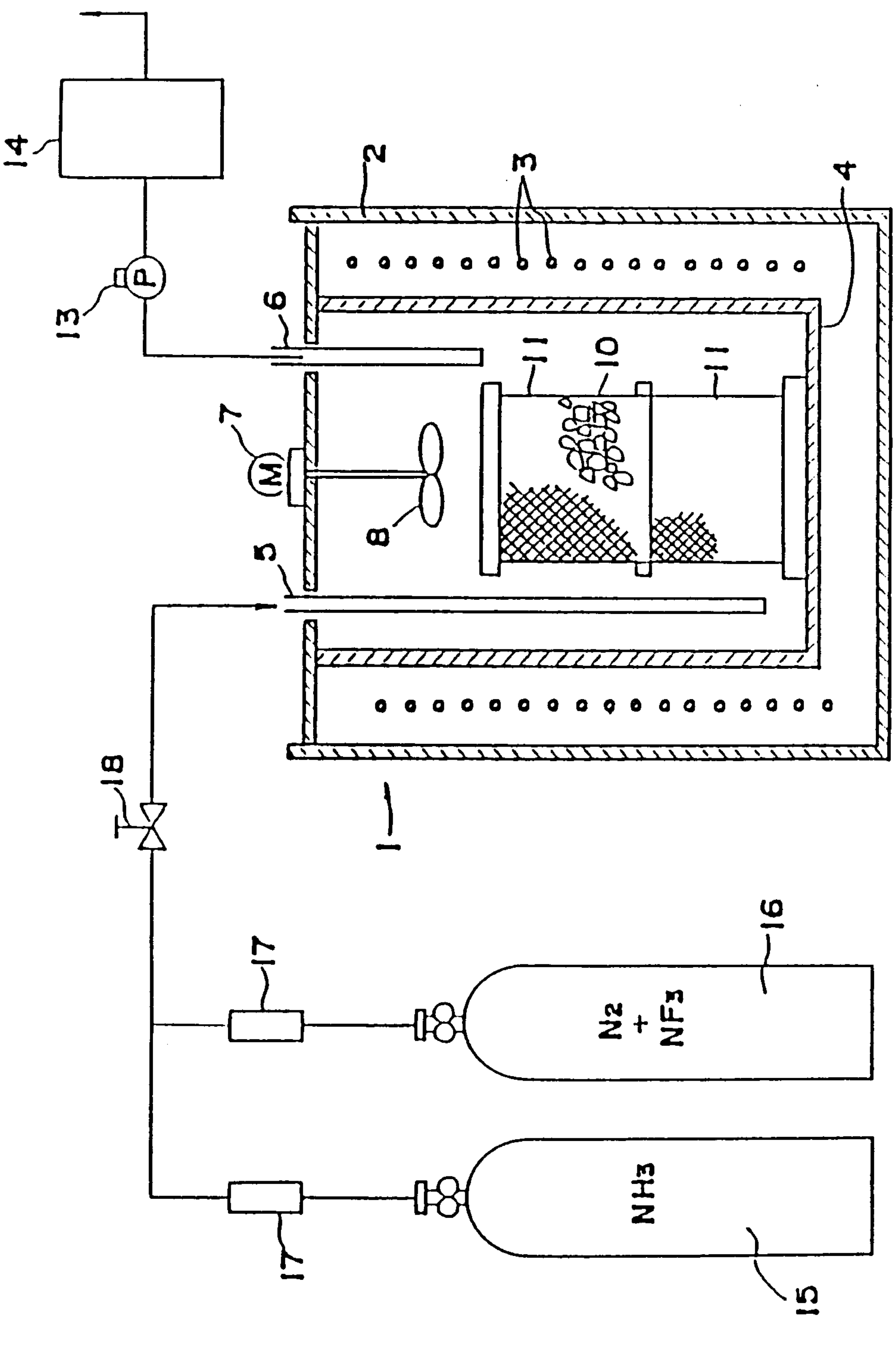
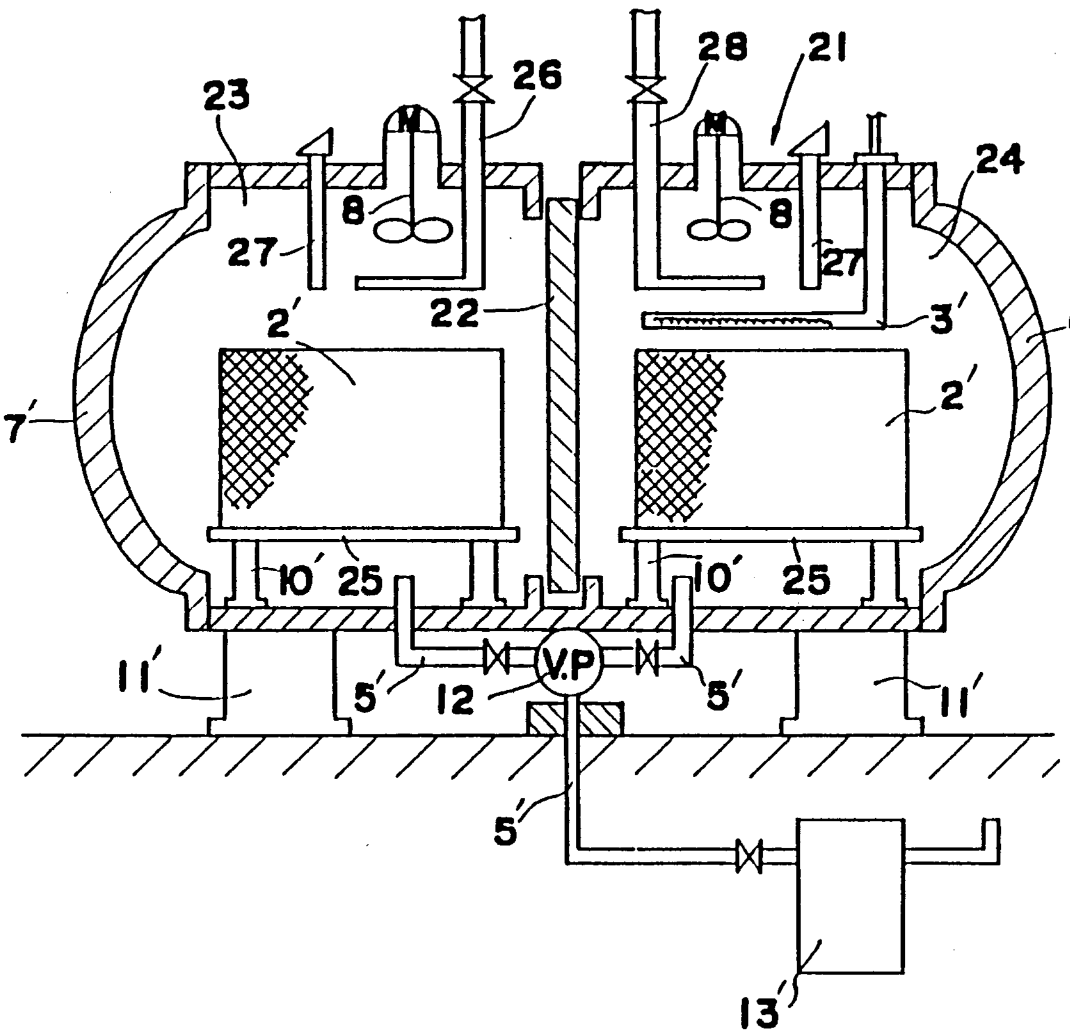
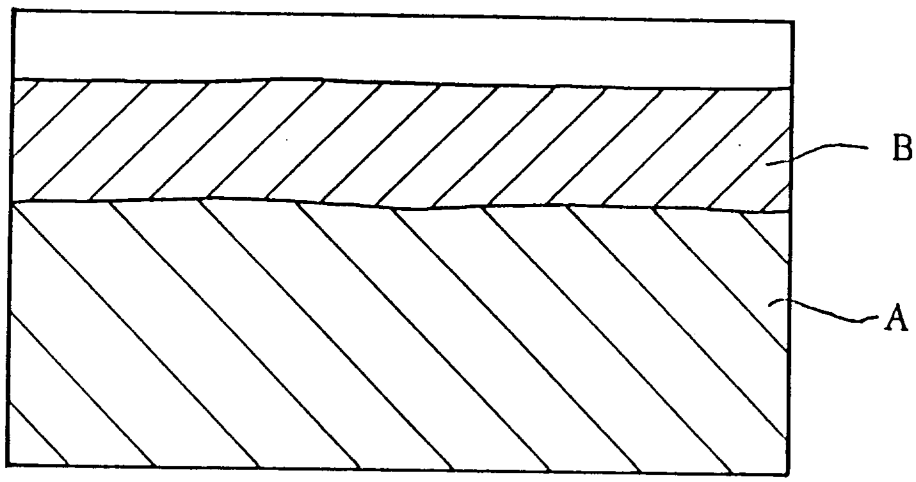


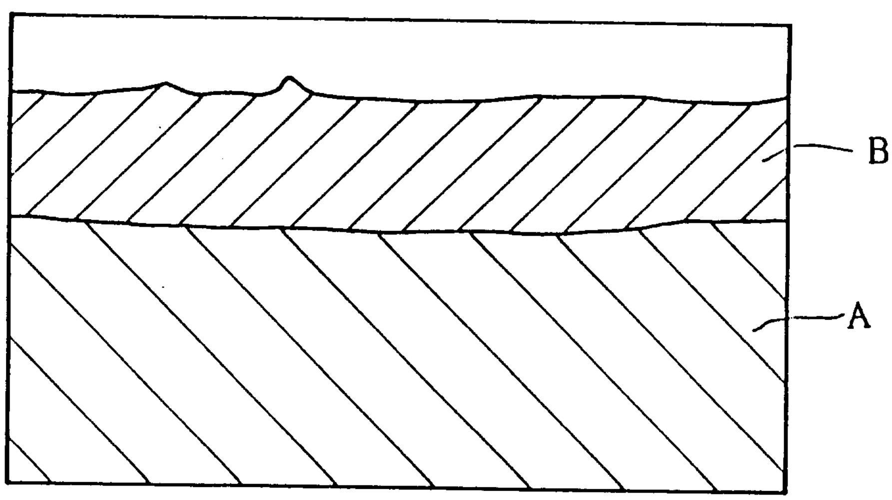
FIG. 1



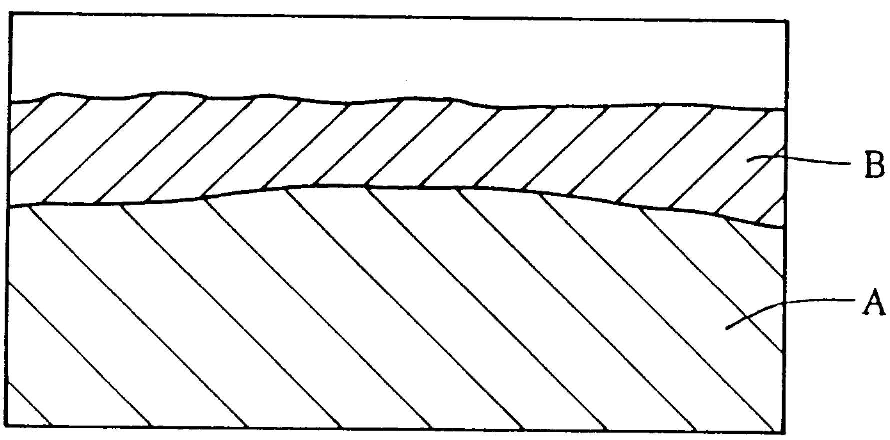
F I G. 2



F I G. 3



F I G. 4



F I G. 5

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EUROPEAN SEARCH REPORT

Application Number

EP 92 30 2169

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	EP-A-0 408 168 (DAIDOUSANSO) * page 5, line 36 - line 43 * * page 6, line 12 - line 46; claims 1-17 * ---	1-5	C23C8/34
A	EP-A-0 352 061 (HASHIMOTO CHEMICAL INDUSTRIES) * page 4, line 8 - line 13 * * page 6, line 39 - line 49; claims 1,3 * ---	1-3	
A	PATENT ABSTRACTS OF JAPAN vol. 8, no. 98 (C-221)(1535) 9 May 1984 & JP-A-59 13 065 (FUJITSU) 23 January 1984 * abstract * ---	1,2	
A	US-A-3 129 124 (DUANE L. BARNEY) * column 4, line 54 - line 61 * -----	1,2	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C23C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	11 NOVEMBER 1992	ELSEN D.B.

CATEGORY OF CITED DOCUMENTS

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