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(54) **A hard austenitic stainless steel screw and a method for manufacturing the same.**

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n2

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Description

This invention relates to a method for manufacturing a hard austenitic stainless steel article, for example a screw or bolt, which has excellent corrosion resistance.

Generally, an austenitic stainless steel is higher in corrosion resistance against acid or salt compared than a carbon steel. However, in surface hardness and strength, it is inferior to carbon steel. Therefore, it has not been proper to use austenitic stainless steel for a screw which particularly needs to be able to tighten to an iron-based plate by self-tapping, such as a tapping screw, a self-drilling screw or a dry wall screw. For these purposes, plated carburized iron articles or 13 Cr stainless steel articles are used. However, these articles are not only inferior in oxidation resistance (rust resistance) to austenitic stainless steel articles but are also weak in their tightening function because of corrosion of their base material by acid rain, which is a major environmental problem of today. Austenitic stainless steel articles are far superior in acid resistance. Accordingly, the present inventors provided new technology for maintaining the tapping property as well as carburized iron articles by nitriding-hardening the austenitic stainless steel screw (Japanese Patent Application No. 177660/1989).

According to this technology, a nitrided hard layer with which even a thick iron plate can be drilled and tapped self-forcedly is formed over the entire surface of the austenitic stainless steel screw. However, this new technology has a serious defect in that the so formed nitrided hard layer lacks the corrosion resistance characteristic of austenitic stainless steel. For example, when using an austenitic stainless steel screw having such a nitrided hard layer, the screw head, exposed to the atmosphere, readily rusts. Generally, when using (tightening) a screw, its head and the neighbourhood of the head are visible, and are exposed to the atmosphere. An austenitic stainless steel screw is devalued as commercial goods by even a bit of change in the color of its head because of rust. It is possible to conduct plating or color-painting on the surface of a nitrided hard layer after nitriding in order to prevent rust from being generated there. However, this is only a temporary solution, not a fundamental one. So as to protect the screw head or the like against nitriding, it was proposed to apply some methods, such as copper-plating and a masking by flame coating, to these parts prior to nitriding. Even if such methods are employed, it is difficult to completely prevent nitriding on the surface of the portion of the austenitic stainless steel base.

FR 2 404 142 discloses a method of forming a nitrided layer over only part of a corrosion-resistant steel screw comprising forming a substantially gas-imperious metallic layer on the part of the screw which is not to be hardened, which metallic layer may be removed after the hardening treatment.

Accordingly, it has been desired to provide a hard austenitic stainless steel screw which has the same tapping property and the like as a carburized iron screw, and to improve the corrosion resistance of the visible parts thereof exposed to the atmosphere, in use, such as the head, to avoid rust and the like.

To accomplish the above-mentioned purpose, the invention provides a method for manufacturing a hard austenitic stainless steel article comprising forming a nitrided hard layer on the surface of an austenitic stainless steel article and removing the nitrided hard layer from predetermined parts of the nitrided article to expose unnitrided stainless steel.

During the process of accumulated research into prevention of rust on the head and the like of an austenitic stainless steel screw, the inventors had the idea to remove a nitrided hard layer from the head or the like, and conducted a series of tests to assess the idea. As a result, they found that even if the nitrided hard layer was removed from the head or the like of the screw, its tapping and drilling functions, which had been improved by nitriding, did not deteriorate and, what was more, corrosion resistance was improved. A nitrided hard layer of the austenitic stainless steel screw has a thickness of 30 to 200 μm in general, preferably 40 to 80 μm for improving tapping and drilling functions. Sixty to seventy percent of the thickness of the nitrided hard layer comprises an alloy layer (surface layer) including a large amount of intermetallic compounds such as CrN and Fe_xN_y , and a diffused layer (inner layer) of a solid solution of N and C. The alloy layer formed on the very surface of the nitrided hard layer suffers from severe deterioration in corrosion resistance due to a considerable decrease in concentration of solid soluble Cr. On the other hand, an inner diffused layer is superior to the alloy layer in corrosion resistance, but not sufficiently good compared with a pure austenitic stainless base of the core portion. For example, in the case of forming a nitrided hard layer by nitriding, it takes 4 to 8 hours for the surface of the nitrided hard layer to rust in a neutral salt spray test, 500 to 700 hours for a diffused layer after removing the alloy layer from the nitrided hard layer to rust, and over 2000 hours for a pure austenitic base per se exposed by removal of the entire thickness of the nitrided layer to rust. This means that corrosion resistance can be improved without deterioration in the tapping and drilling properties, which were strengthened by

nitriding, when the nitrided hard layer is removed from the screw head and the like, exposed to the atmosphere in a tightened state.

The invention will be further described, by way of example, with reference to the drawings, in which

Fig. 1 shows a front view of an austenitic stainless steel self-drilling screw according to the invention;

Fig. 2 shows a cross-sectional view illustrating an example of a nitriding furnace for carrying out a method according to the invention; and

Fig. 3 shows an explanatory view illustrating an example in which the nitrided hard layer over predetermined portions of a screw is removed.

In this invention, of the nitrided hard layer formed over the entire surface of an austenitic stainless steel screw, the nitrided layer formed on the screw head, a neck portion, and the like of the screw which are in contact with the atmosphere when tightened is removed. Austenitic stainless steel base is exposed where the nitrided layer is removed to achieve rust prevention and corrosion resistance characteristic of austenitic stainless steel *per se*.

The nitrided hard layer formed over the entire surface of the austenitic stainless steel screw comprises an alloy layer, which is a surface layer, and a diffused layer, which is an inner layer, as mentioned above. In general, the alloy layer has a thickness of 15 to 50 μ m and a surface hardness (Hv) of 750 to 1400 and the inner diffused layer has a thickness of 20 to 100 μ m and a surface hardness (Hv) of 320 to 650.

In this invention, the nitrided hard layer, comprising an alloy layer and a diffused layer, of the screw head portion and the like is removed from part of the surface of the screw.

Methods of removal include a chemical method such as a dipping treatment in which the screw head and the like of the austenitic stainless steel screw are dipped in a mixed acid, for example, HCl + HNO₃ or HF + HNO₃, or in a single acid solution of HNO₃ heated to about 60°C, and a mechanical method such as scouring.

In the case of removing the nitrided hard layer by a chemical method, masking is conducted before dipping in acid on the portion over which the nitrided layer is to remain, with a coating agent not denatured by acid, or only the head and neck portions of the austenitic stainless steel screw are dipped in the acid. In this case, it is possible to appropriately control the kind and concentration of acid, the temperature, and the dipping time according to the condition of the nitrided hard layer which is to be removed. This method of removing the nitrided hard layer has the advantage that the portion to be removed of the nitrided hard layer is

selected voluntarily.

When the nitrided hard layer is removed in this way, the diameters of some portions of the austenitic stainless steel screw, such as the screw head and the neck part, from which the nitrided hard layer is removed, are relatively small. To allow for this, the diameters of the screw head and the neck part connected thereto are advantageously designed to be larger by the thickness of the nitrided hard layer. In this way, there is no deterioration in the breaking torque and thus no decrease in the tightening function of the screw.

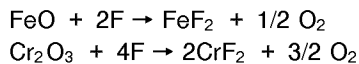
Examples of the manufacture of a hard austenitic stainless steel screw according to the present invention are described in detail as follows.

An austenitic stainless screw is held preliminarily in a fluorine- or fluoride-containing gas atmosphere to form a fluorinated layer on the steel surface, then heated in a nitriding atmosphere to remove the fluorinated layer and at the same time to convert the surface (the surface layer of the screw) to a nitrided layer. The nitrided layer over predetermined parts of the screw is removed to prevent rust on those parts.

The term "fluorine- or fluoride-containing gas" used in the pretreatment prior to nitriding means a dilution of at least one fluorine source component selected from NF₃, BF₃, CF₄, HF, SF₆, F₂, CH₂F₂, CH₃F, C₂F₆, WF₆, CHF₃, SiF₄ and the like in an inert gas such as N₂. Among these fluorine source components, NF₃ is most suitable for practical use since it is superior in reactivity, ease of handling and other aspects to the others. The screws are held in the above-mentioned fluorine- or fluoride-containing gas atmosphere at a temperature of, for example, 250 to 400°C in the case of NF₃, for a preliminary treatment of the surface of an austenitic stainless screw and then subjected to nitriding (or carbonitriding) using a known nitriding gas such as ammonia. When F₂ gas alone or a mixed gas composed of F₂ gas and an inert gas is used as the fluorine- or fluoride-containing gas the above-mentioned holding temperature is arranged in the range of 100°C to 250°C. The concentration of the fluorine source component, such as NF₃, in such fluorine- or fluoride-containing gas should amount to, for example, 1,000-100,000ppm, preferably 20,000-70,000ppm, more preferably 30,000-50,000ppm. The holding time in such a fluorine- or fluoride-containing gas atmosphere may appropriately be selected depending on the steel species, geometry and dimensions of the screws, the heating temperature and so forth, and is generally within the range of ten and odd minutes or scores of minutes.

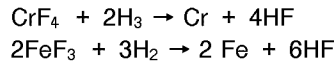
To be more concrete in illustrating the aforementioned pretreatment using a fluorine- or fluoride-containing gas and the nitriding treatment,

austenitic stainless screws X having a head portion A, a neck portion B and a thread portion C as shown in Fig. 1, for instance, are degreased and then charged into a heat treatment furnace 1 such as shown in Fig. 2. This furnace 1 is a pit furnace comprising an inner vessel 4 surrounded by a heater 3 disposed within an outer shell 2, with a gas inlet pipe 5 and an exhaust pipe 6 therein. Gas is supplied from cylinders 15 and 16 via flow meters 17, a valve 18 and the like into the gas inlet pipe 5. The inside atmosphere is stirred by means of a fan 8 driven by a motor 7. The screws X placed in a metallic container 11 are charged into the furnace. In Fig. 2, the reference numeral 13 indicates a vacuum pump and 14 a noxious substance eliminator. A fluorine- or fluoride-containing reaction gas, for example, a mixed gas composed of NF_3 and N_2 , is introduced into this furnace and heated, together with the works, at a predetermined reaction temperature. At temperature of 250-400 °C, NF_3 evolves fluorine in the nascent state, whereby the organic and inorganic contaminants on the surface of the screws are eliminated therefrom and at the same time this fluorine rapidly reacts with the base elements Fe and chromium on the surface and/or with oxides on the steel work surface, such as FeO , Fe_3O_4 and Cr_2O_3 . As a result, a very thin fluorinated layer containing such compounds as FeF_2 , FeF_3 , CrF_2 , CrF_4 and the like in the metal composition is formed on the surface, for example as follows:



These reactions convert the oxidized layer on the surface of the screws X to a fluorinated layer. At the same time, O_2 adsorbed on the surface is removed therefrom. Where O_2 , H_2 and H_2O are absent, such fluorinated layer is stable at temperature up to 600 °C and it is considered that the stable fluorinated layer prevents oxidized layer formation on the metal bases and absorption of O_2 thereon until the subsequent step of nitriding. A fluorinated layer, which is similarly stable, is formed on the furnace material surface as well and minimizes damage to the furnace material surface.

The screws X thus treated with such fluorine- or fluoride-containing reaction gas are then heated at a nitriding temperature of 480 °C-700 °C. Upon addition of NH_3 or a mixed gas composed of NH_3 and a carbon source gas (e.g. RX gas) in said heated condition, the fluorinated layer undergoes reduction or destruction by means of H_2 or a trace amount of water to give an active metal base comprised of austenitic stainless steel, as shown, for example, by the following reaction equations:



Upon formation of such active metal base, active N atoms are adsorbed thereon, then enter the metal structure and diffuse therein and, as a result, a chemical compound layer (a nitrided hard layer) containing such nitrides as CrN , Fe_2N , Fe_3N and Fe_4N is formed on the surface.

The obtained nitrided hard layer comprises an alloy layer and a diffused layer and covers all the screw X shown in Fig. 1. This invention allows removal of the nitrided hard layer from, for example, the whole head portion A and a part of the neck portion B of the screw X shown in Fig. 1, while leaving the nitrided hard layer on the thread portion C and rest of the neck portion B as they are. The removal is, for example, conducted by heating HNO_3 -HF solution at about 50 °C, dipping the whole head portion A and a part of the neck portion B of the screw therein for about 10 to 120 minutes to melt and remove the nitrided hard layer. It is efficient to remove the nitrided layer chemically, but in some cases, removal may be conducted by scouring with a scourer or the like. In the screws to which the removal treatment is conducted, the nitrided hard layer of the whole head portion and a part of the neck portion is removed in this way to expose austenitic stainless steel. By this treatment, the screw X has sufficient corrosion resistance, resulting from that of austenitic stainless steel per se. The remaining nitrided hard layer of part of the neck portion B and the thread portion C has significantly improved hardness compared with that of austenitic stainless steel, giving the screw the same excellent tapping and tightening functions as carburized iron articles.

The present invention has been described using a screw as an example so far, but a bolt is also included in the term screw. In the afore-mentioned description, nitriding is conducted by using NH_3 or a mixed gas comprising NH_3 and a gas containing a carbon source, but nitriding by glow discharge or by salt bath may be substituted for this type of nitriding.

Example 1

Cross recessed head tapping screws of SUS305, austenitic stainless steel (4.2mm ϕ x 19mm) were cleaned with trichloroethylene, then charged into a treatment furnace 1 as shown in Fig. 2, and held at 380 °C for 15 minutes in an N_2 gas atmosphere containing 5,000ppm of NF_3 for fluoriding, then heated at 530 °C, and nitriding treatment was carried out at that temperature for 3 hours while a mixed gas composed of 50% NH_3 plus 50% N_2 (hereinafter: % by volume) was introduced

into the furnace. The works were then air-cooled and taken out of the furnace. The thus obtained screws had a nitrided hard layer with thickness of 40 μ m overall. The nitrided screw except for the head portion and a part of the neck portion to 4mm below the head was coated with vinyl chloride resin liquid and dried, to cover the screw with the coating. The screw was then dipped in 10% solution of HNO₃ at 63°C for 15 minutes, taken out, washed with water and dried. As a result, the surface hardness (Hv) of the part of the tapping screw masked by the coating (mainly the thread) was 1000 to 1100. In contrast, the head of the tapping screw from which the nitrided hard layer had been removed by the acid treatment had a surface hardness of 340 to 380. A salt spray test (Corrosion acceleration test) was conducted on the tapping screw and it was found that rust was not caused even after 2000 hours on the head and the part of the neck portion on which the austenitic stainless steel base was exposed. On the contrary, it was found that rust was caused after 6 hours on the part (mainly the thread) from which the nitrided hard layer was not removed. A drilling test was conducted on the above-mentioned screw and it was found that it had the same property as a conventional tapping screw (carburized iron steel works).

Example 2

Self drilling screws of SUS 305, austenitic stainless steel (hexagon head, 4.8mm ϕ x 25mm) were nitrided as in Example 1. In this case, the nitrided hard layer was formed over the entire self-drilling screw; its thickness was 55 μ m. The nitrided screw, except for the head and a part of the neck to 5mm below the head was dipped in vinyl chloride resin liquid and dried to cover the screw with a coating. Then a plurality of the screws were screwed into a polystyrene resin plate having a thickness of 30mm as shown in Fig. 3. The resin plate was floated upside down on strong acid solution (HNO₃ : HCl=3:1), taken out after 5 minutes and floated on a 10% HNO₃ solution at 60°C for 10 minutes. Then the self-drilling screws were taken from the polystyrene resin plate, washed with water and dried. The dried screws were plated with zinc by a conventional plating method. A drilling test on the thus obtained screws was conducted against a steel plate with a thickness of 3.2mm (SPCC). Average drilling time in this case was 3.1 seconds. The time could be shortened by 20% on average compared with a conventional self-drilling screw (carburized iron works). The result of a salt spray test was the same as in Example 1.

Example 3

Self-drilling screws of austenitic stainless steel (hexagon head, 6.3mm ϕ x 150mm) as shown in Fig. 1 were nitrided as in Example 1. The thus obtained self-drilling screw was covered with a nitrided hard layer overall; the thickness thereof was 75 μ m. The nitrided screw except for the head and a part of the neck portion to 100mm below the head was dipped in vinyl chloride resin liquid and dried to cover the screw with coating. Then the screw was dipped in strong acid solution (HNO₃ : HCl=3:1) at 45°C for 5 minutes and additionally dipped in a solution with 10% HNO₃ at 60°C for 5 minutes, taken out, washed with water and dried. A salt spray test was conducted on the thus treated screw and the same result as in Example 1 was obtained, and the result of drilling test was the same as in Example 2. The breaking torque value of the thus obtained austenitic stainless self-drilling screw was examined. The value was lower by 7% than the austenitic stainless steel self-drilling screw the whole surface of which was covered by a nitrided hard layer, without the acid dipping treatment. In order to avoid the deterioration of the breaking torque value, austenitic stainless steel self drilling screws of which the diameters of the screw head and the neck portion were relatively large (about 150 μ m) were manufactured. They were nitrided and then dipped in acid to remove the nitrided hard layer from the screw head portion and neck portion. After eliminating the nitrided hard layer of the head and neck portions, the diameters of the head and neck portions were decreased.

The breaking torque value of such screws was equal to an austenitic stainless steel self-drilling screw the whole surface of which was covered with a nitrided hard layer and the whole part having a diameter as previously designed respectively.

As mentioned above, in the austenitic stainless steel screw according to the present invention, a nitrided hard layer is removed from predetermined portions such as the head and neck portion, so that the austenitic stainless steel base is exposed on these portions. The head portion is exposed to the atmosphere in a tightened state and is affected by acid rain and the like, and the neck portion is in contact with acid rain and the like which has penetrated from outside. The portions from which the nitrided layer is removed maintain a good anti-corrosion property comparable with that of the austenitic stainless steel itself. On the other hand, in the thread portion, the hardness and the like are greatly improved by the nitrided hard layer, so that surface hardness and strength become approximately equal to those of carbon steel products, so that they are able to tap and tighten by themselves.

In the method according to the present invention, prior to nitriding the above-mentioned austenitic stainless steel screw, the screw is advantageously held in a fluorine- or fluoride-containing gas atmosphere to form a fluoride layer on the surface thereof. In that state the screw is nitrided, so that the formed nitrided layer is uniform and deep to give a hard austenitic stainless steel screw having good surface properties.

Claims

1. A method for manufacturing a hard austenitic stainless steel article comprising: forming a nitrided hard layer on the surface of an austenitic stainless steel article and removing the nitrided hard layer from predetermined parts of the nitrided article to expose unnitrided stainless steel.
2. A method according to claim 1 in which the nitrided hard layer is formed by heating the austenitic stainless steel article in a nitriding atmosphere.
3. A method according to claim 1 or 2 in which the austenitic stainless article is held in an atmosphere of fluorine- or fluoride-containing gas to form a fluoride layer on its surface and then the fluorided article is heated in a nitriding atmosphere to form a nitrided hard layer on the surface of the stainless steel article.
4. A method according to any preceding claim in which the removal of the nitrided hard layer is achieved by contacting the nitrided layer with strong acid.

Patentansprüche

1. Verfahren zur Herstellung eines harten Gegenstandes aus austenitischem rostfreien Stahl, umfassend: Bildung einer nitrierten harten Schicht an der Oberfläche eines Gegenstandes aus austenitischem rostfreien Stahl und Entfernen der nitrierten harten Schicht von vorbestimmten Abschnitten des nitrierten Gegenstandes um unnitrierten rostfreien Stahl freizulegen.
2. Verfahren nach Anspruch 1, bei dem die nitrierte harte Schicht durch Erhitzen des Gegenstandes aus austenitischem rostfreien Stahl in einer nitrierenden Atmosphäre gebildet wird.
3. Verfahren nach Anspruch 1 oder 2, bei dem der Gegenstand aus austenitischem rostfreien Stahl in einer Atmosphäre von fluor- oder fluo-

ridhaltigem Gas gehalten wird, um eine Fluoridschicht auf seiner Oberfläche zu bilden und dann der fluoridierte Gegenstand in einer nitrierenden Atmosphäre erhitzt wird, um eine nitrierte harte Schicht auf der Oberfläche des Gegenstandes aus rostfreiem Stahl zu bilden.

4. Verfahren nach irgendeinem der vorhergehenden Ansprüche, bei dem die Entfernung der nitrierten harten Schicht durch Kontaktierung der nitrierten harten Schicht mit einer starken Säure bewirkt wird.

Revendications

1. Procédé de fabrication d'un article en acier inoxydable austénitique dur, comprenant les étapes consistant à : former une couche dure nitrurée à la surface d'un article en acier inoxydable austénitique, et éliminer la couche dure nitrurée dans des parties prédéterminées de l'article nitruré, pour mettre à nu l'acier inoxydable non nitruré.
2. Procédé selon la revendication 1, dans lequel la couche dure nitrurée est formée en chauffant l'article en acier inoxydable austénitique dans une atmosphère nitrurante.
3. Procédé selon la revendication 1 ou 2, dans lequel l'article en acier inoxydable austénitique est maintenu dans une atmosphère de gaz contenant du fluor ou un fluorure, pour former une couche de fluorure à sa surface, puis l'article fluoré est chauffé dans une atmosphère nitrurante pour former une couche dure nitrurée à la surface de l'article en acier inoxydable.
4. Procédé selon l'une quelconque des revendications précédentes, dans lequel l'élimination de la couche dure nitrurée est réalisée en mettant la couche nitrurée en contact avec un acide fort.

FIG.1

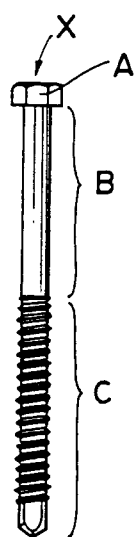


FIG.2

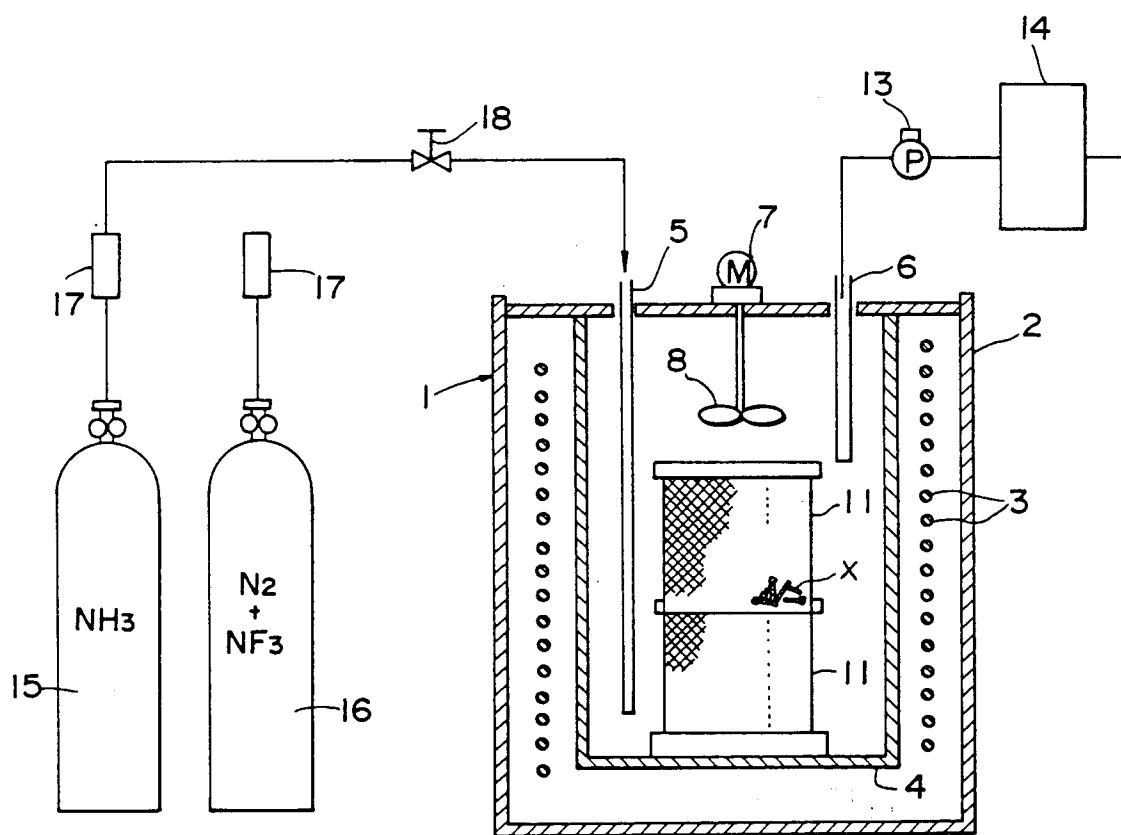


FIG.3

