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(54) PROCESS FOR FORMING PASSIVE FILM ON STAINLESS STEEL, AND STAINLESS STEEL AND GAS- AND LIOUID-CONTACTING PART.

(57) A process for forming a passive film excellent in degasifiability and corrosion resistance by making the film extremely flat and dense. The process comprises subjecting the surface of stainless steel to electrolytic polishing, oxidation in an oxidative atmosphere and removal of iron oxide formed thereon by reduction with hydrogen.

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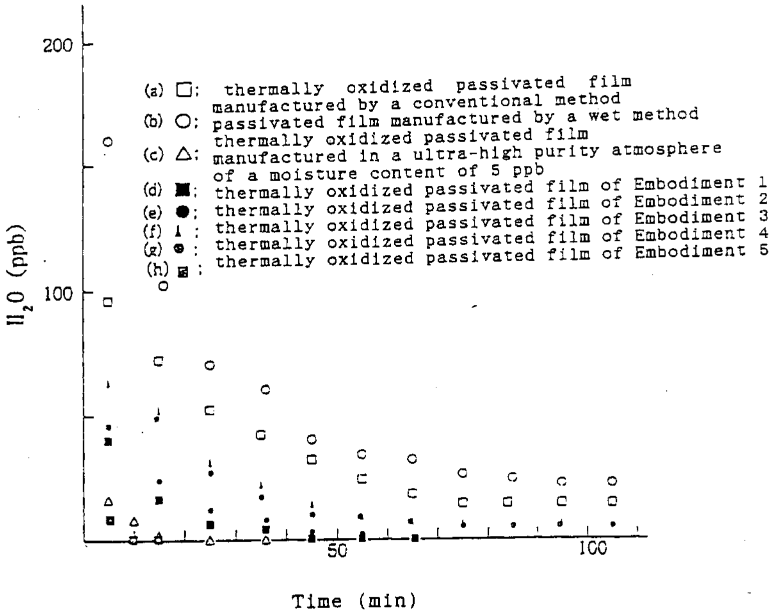
FIG 1


(a) □: thermally oxidized passivated film manufactured by a conventional method
(b) ○: passivated film manufactured by a wet method
(c) △: thermally oxidized passivated film manufactured in a ultra-high purity atmosphere of a moisture content of 5 ppb
(d) ■: thermally oxidized passivated film of Embodiment 1
(e) ●: thermally oxidized passivated film of Embodiment 2
(f) ⫯ : thermally oxidized passivated film of Embodiment 3
(g) ⊕ : thermally oxidized passivated film of Embodiment 4
(h) ▣ : thermally oxidized passivated film of Embodiment 5
200
100
H_2O (ppb)
50
100
Time (min)

TECHNICAL FIELD

The present invention relates to a method for forming stainless steel passivated films, stainless steel, and gas-contacting and liquid-contacting parts, and in particular relates to a method for forming passivated films of oxidized passivated stainless steel, as well as stainless steel, and gas-contacting and liquid-contacting parts which can be preferably applied to ultra-high vacuum apparatuses, ultra-high clean apparatuses, ultra-pure water apparatuses and the like.

BACKGROUND ART

Recently, a technique for realizing ultra-high vacuum, or a technique for allowing a small amount of predetermined gas in a vacuum chamber to produce a ultra-high clean pressure-reduced atmosphere has become extremely important. These techniques are widely used for research on material characteristics, formation of various thin films, production of semiconductor devices and the like, and consequently higher degrees of vacuum have been increasingly realized, however, further it is extremely strongly desired to realize a pressure-reduced atmosphere in which contamination of impurities is decreased to the limit.

For example, as exemplified by semiconductor devices, the size of a unit element becomes small year by year in accordance with high integration of LSI, and research and development for semiconductor devices having a size of 1 μm to sub micron, and further 0.5 μm or below is being actively performed directing realization of practical use.

In the production of such semiconductor devices, a step of forming a thin film, a step of etching the formed thin film into a predetermined circuit pattern and the like are repeatedly performed. And it is common that these processes are performed in a ultra-high vacuum state, or in a pressure-reduced atmosphere in which predetermined gas is introduced. If these steps are contaminated by impurities, problems are caused such that, for example, the film quality of thin films to be formed is deteriorated, the accuracy of fine processing is not obtained and the like. This is the reason why the ultra-high vacuum and the ultra-high clean pressure-reduced atmosphere are required.

As one of the most important causes which have been obstructed the realization of the ultra-high vacuum and the ultra-high clean pressure-reduced atmosphere until now, the gas released from the surface of stainless steel widely used for chambers and pipe arrangements may be pointed out. Especially, the moisture absorbed to the stainless surface which disengages in the vacuum or the pressure-reduced atmosphere has served as the most important pollution source.

Fig. 16 is a graph showing the relation between the gas pollution and the total leak amount of a system including a gas pipe arrangement line and a reaction chamber (the sum of the external leak and the release gas amount from the inner surface of the pipe arrangement line and the reaction chamber) in a conventional apparatus. A plurality of lines in the figure show the relation between the impurity concentration in the atmosphere and the total leak amount of the system with respect to cases in which the flow rate of gas is changed to various values.

The semiconductor process is in a tendency that the flow rate of gas is more and more decreased in order to realize a process having higher accuracy, and for example, it becomes common to use a flow rate of 10 cc/min or less. As understood from Fig. 16, when a flow rate of 10/min is used (symbol ∇), if there is a system total leak of a degree of 10^{-3} to 10^{-6} Torr•l/sec as in apparatuses widely used at present, the impurity concentration in the gas becomes 10 ppm to 1 %, which is far from a high clean process.

The present inventors have invented a ultra-high clean gas supply system, and succeeded to suppress the leak amount from the outside of the system to be not more than 1 x 10^{-11} Torr•l/sec which is the detection limit of a detector in the present circumstance. However, there is leak from the inside of the system, that is the above-mentioned gas release from the surface of stainless steel, so that consequently it was impossible to lower the impurity concentration in the pressure-reduced atmosphere.

The minimum value of the surface release gas amount obtained by the surface treatment in the present ultra-high vacuum technique is 1 x 10^{-11} Torr•l/sec•cm^2 in the case of stainless steel. In this case, even when the surface area exposed at the inside of the chamber is estimated to be, for example, 1 m^2 which is the smallest, a leak amount of 1 x 10^{-7} Torr•l/sec is given as a total, and consequently in the case of a gas flow rate of 10 cc/min, gas having a purity of an impurity concentration of about 1 ppm is only obtained. It is needless to say that when the gas flow rate is made further small, the purity further drops.

Therefore, in order to lower the disengaged gas component from the chamber inner surface to be in the same degree as 1 x 10^{-11} Torr•l/sec which is the same as the external leak amount of the system, it is necessary to make the degassing from the surface of stainless steel to be not more than 1 x 10^{-15} Torr•l/sec•cm^2. Thus, a treatment technique for the stainless steel surface for decreasing the gas release amount has been strongly demanded.

On the other hand, in the semiconductor production process, various gases ranging from relatively stable general gases (O_2, N_2, Ar, H_2, He) to special gases having strong reactivity, corrosion property and toxicity are used. Especially, among the special gases, there are gases which generate hydrochloric acid or hydrofluoric acid exhibiting a strong corrosion property when moisture exists in the atmosphere such as for example hydrogen chloride (HCl), chlorine (Cl_2), trichloroboron (BCl_3), trifluoroboron (BF_3) and the like. Usually, stainless steel is often used for pipe arrangements and chamber materials for handling these gases because of corrosion resistance, high strength, easiness of secondary processing, easiness of welding, and easiness of polishing treatment for the inner surface.

The stainless steel is excellent in corrosion resistance in a ultra-high purity atmosphere of an extremely minute amount of moisture, however, it is easily corroded in a chlorine type or a fluorine type gas atmosphere in which moisture exists. Thus, a treatment for corrosion resistance becomes indispensable after the surface polishing of stainless steel.

As the treatment method, there is Ni-W-P coating (cleanness coating method) for coating the stainless steel with metal having strong corrosion resistance, or a passivated film formation method in which a thin oxide film is made on the metallic surface in a nitric acid solution and the like.

However, they are wet methods, so that a lot of remaining residues of the moisture and the treatment solution exist on the film surface, in the film and at the boundary between the film and stainless, and they do not become capable of application to ultra-high vacuum apparatuses, ultra-high clean apparatuses and the like.

Thus, a method has been proposed in which stainless steel is oxidized in a gaseous phase so as to form a passivated film.

As a result of repeated research by the present inventors on the relation between degassing characteristics of oxidized passivated films and formation conditions thereof, it has been elucidated that the moisture in the oxidizable atmosphere during passivated film formation greatly affects the surface state and the degassing characteristic of the passivated film, and following knowledge has been obtained in relation thereto.

As shown in Fig. 1 (a), an oxidized passivated film formed in a high purity atmosphere having a moisture content of, for example, about 100 ppb is improved in the degassing characteristic as compared with a passivated film formed by the wet method ((b) in Fig. 1). However, the degassing characteristic was not sufficient yet, which could not result in the use as a material for ultra-high vacuum or ultra-high clean pressure-reduced apparatuses.

Concentration profiles of each of component atoms in the depth direction in which this passivated one was measured by XPS (X-ray photoelectron spectroscopy) are shown in Fig. 17, and scanning type electron microphotographs of the film surface are shown in Fig.18. As can be seen in the electron microphotographs in Fig. 18, a large number of cracks and pin holes are observed on the surface of the passivated film, and a smooth and close film is not obtained. In addition, as shown in Fig. 16, it has been found that little chromium oxide having high corrosion resistance exists at the outermost surface of the passivated film in which a layer containing iron oxide as a main component is formed.

As described above, when the oxidized passivated film is formed in the oxidizable atmosphere containing moisture, the smoothness and closeness of the passivated film obtained are affected depending on the moisture concentration in the atmosphere even in the case of an extremely minute amount of the moisture, and the cracks and pin holes are generated in the passivated film. In addition, according to the analysis by XPS, it has been found that these cracks, pin holes and the like exist in the layer containing much iron oxide at the outermost surface, and the degassing characteristic is deteriorated because the moisture is absorbed and occluded by these cracks, pin holes and the like.

On the other hand, when an oxidized passivated film is formed on the stainless steel surface in a ultra-high purity atmosphere having a moisture amount of 10 ppb or below, the passivated film having excellent degassing characteristic is obtained as shown in Fig. 1 (c), which can be used as a material for ultra-high vacuum or ultra-high clean pressure-reduced apparatuses, however, this passivated film also does not achieve at a degree in which surface irregularity can be completely neglected.

That is to say, electrolytic polishing is performed before the formation of the passivated film in order to smooth the surface, however, the surface roughness which can be achieved by the electrolytic polishing at present has a limit of R_{max}:0.05-0.1 μm, and usually a surface roughness of 0.5 μm is used. However, when the formation of the passivated film is performed after the electrolytic polishing, the surface roughness during the electrolytic polishing is not maintained, and the surface becomes rough. For example, even if the surface of a base material (bulk portion) is finished to have R_{max}: 0.05-0.1 μm before the formation of the passivated film, the surface roughness of the passivated film becomes rougher than R_{max}: 0.1 after the passivated film is formed. Consequently, stainless steel formed with a passivated film in which R_{max} is below 0.1 for the surface roughness does not exist at present. And the present inventors have elucidated that the surface roughness of the passivated film greatly affects the degassing characteristic, and the rougher the surface roughness is, the more the gas release amount is.

The present invention has been made on the basis of the finding of the above-mentioned problems with respect to the oxidized passivated film.

It is an object of the present invention to achieve realization of ultra-flatness and closeness of the passivated film, and provide a method for forming passivated films of stainless steel excellent in degassing characteristics and corrosion resistance, as well as stainless steel, and gas-contacting and liquid-contacting parts.

DISCLOSURE OF THE INVENTION

The first gist of the present invention lies in a method for forming stainless steel passivated films characterized in that the surface of stainless steel is subjected to an electrolytic polishing treatment, thereafter an oxidation treatment is performed in oxidizable atmospheric gas, and subsequently iron oxide on the surface is reduced and removed using hydrogen gas.

The second gist of the present invention lies in a method for forming stainless steel passivated films characterized in that the surface of stainless steel is subjected to an electrolytic polishing treatment, thereafter welding is performed, an oxidation treatment is performed in oxidizable atmospheric gas after the welding while heating a welded portion, and then iron oxide on the surface is reduced and removed using hydrogen gas.

The third gist of the present invention lies in stainless steel characterized in that it has a passivated film in which R_{max} is 0.1 μm or below for the surface roughness.

The fourth gist of the present invention lies in a gas-contacting part and a liquid-contacting part characterized in that they have on the surface a stainless steel passivated film formed such that the surface of stainless steel is subjected to an electrolytic polishing treatment, thereafter an oxidation treatment is performed in oxidizable atmospheric gas, and subsequently iron oxide on the surface is reduced and removed using hydrogen gas.

FUNCTION AND EMBODIMENT EXAMPLES

The function of the present invention will be explained hereinafter together with embodiment examples.

(Electrolytic polishing)

In the present invention, the electrolytic polishing is performed before the formation of the passivated film. As an electrolytic polishing method, for example, a combined electrolytic polishing method may be used. The combined electrolytic polishing method is a method in which anodic metal subjected to polishing is electrolyzed and eluted by electrolysis, and a passivated film generated on the surface of the metal subjected to polishing is processed to have a specular face by means of an abrasive action using polishing abrasive grains (for example, official gazette of Japanese Patent Publication No. SHO-57-47759-1982).

By means of the electrolytic polishing of stainless steel, a processed denatured layer on the surface is removed. In addition, it is possible to allow the surface roughness to have R_{max}: 1 μm or below. It is preferable that the surface roughness after the electrolytic polishing is as fine as possible, and hence it is possible to make it to be 0.05-0.1 μm.

The change in the surface state by the electrolytic polishing is shown in Fig. 2. In Fig. 2, Fig. 2 (a) shows a surface state after the polishing, and Fig. 2 (b) shows a surface state before the polishing. As clarified from Fig. 2, large irregularity of crystal grains exists before the polishing, and no continuous film is obtained even when an oxidized passivated film is formed in this state, resulting in a film inferior in corrosion resistance. Further, moisture and the like is occluded and adsorbed between crystal grains, so that no film having a good degassing characteristic is obtained. By means of the application of the electrolytic polishing treatment, the irregularity on the surface disappears, and a smooth face is provided. As a result, the surface area decreases, and the adsorption and occlusion amount of moisture greatly decreases.

Incidentally, it is preferable to perform fine washing and drying after the electrolytic polishing in the same manner as washing of wafers.

(High temperature baking pretreatment)

In the present invention, the passivated film formation treatment may be performed immediately after the electrolytic polishing, however, it is preferable that high temperature baking is performed before the passivated film formation treatment. When the high temperature baking treatment is performed before the passivated film formation treatment, the chromium concentration at the stainless surface side increases, and a passivated film which is close and excellent in corrosion resistance is formed.

The high temperature baking pretreatment is performed, for example, in an inert gas atmosphere such as Ar, He, N_2 gas and the like. The time is preferably 1-10 hours. The treatment temperature is preferably 300-600 °C, and more preferably 400-520 °C. When it is performed in a temperature range of 400-520 °C, the roughness on the surface is further suppressed, an oxidized passivated film formed becomes a closer film as compared with cases of execution in other temperature ranges, and the degassing characteristic is more improved.

Incidentally, the oxidized passivated film is also formed in this high temperature baking treatment. The baking is performed in an inert gas atmosphere. The reason why the oxidized passivated film is formed on the surface irrelevant to the fact that the baking is performed in the inert gas atmosphere (that is to say, an atmosphere containing no oxygen) is not necessarily clear, however, it is considered that a porous oxide layer is formed on the stainless steel surface by the electrolytic polishing, and oxygen in the layer serves as a supply source of oxygen for the passivated film formation. In addition, the surface roughness of the passivated film formed by the high temperature baking maintains a surface roughness after the electrolytic baking. The thickness of this passivated film changes also depending on the baking temperature and time, which becomes, for example, a thickness of about 30Å in the case of 500 °C x 10 hours, so that an exact state after the high temperature baking can be also put to practical use.

(Oxidation treatment - passivated film formation treatment)

Oxidizable gas (for example, mixed gas of Ar/O_2 = 4/1 (molar ratio)) is introduced after the high temperature baking treatment, which is heated to, for example, 350-450 °C to form an oxidized passivated film on the stainless surface. By means of this oxidation treatment, a layer containing much chromium oxide on the stainless surface is formed, and a layer containing much iron oxide is formed thereon. The layer containing much iron oxide is a porous film having cracks and pin holes as described above, The degree of these cracks, pin holes and the like changes depending on the moisture amount in the oxidizable atmosphere, and the more minute the moisture content is, the more preferable it is.

(Hydrogen gas treatment)

The oxidizable gas is exhausted after the passivated film formation treatment, and successively hydrogen gas is introduced to reduce and remove the layer of the passivated outermost surface. By means of this hydrogen treatment, the outermost surface of the passivated film becomes a clean and flat face. This is considered to result from the fact that the layer containing much iron oxide in which the pin holes and crack exist is reduced and removed by hydrogen, and the close layer containing much chromium oxide appears.

It is generally said that hydrogen molecules are subjected to radical formation at a temperature not less than 700 °C to cause a reduction reaction, and the reason why the reduction reaction takes place at a low temperature of about 300 oC has not been confirmed yet, however, it is postulated to be due to the fact that Ni contained in stainless serves as a catalyst. The hydrogen concentration in the hydrogen treatment gas is preferably 0.1 ppm to 10 %, and more preferably 0.5-100 ppm. In the range of 0.5-100 ppm, the close passivated film having a more excellent degassing characteristic is formed. In addition, the temperature for the hydrogen treatment is preferably 200-500 °C, and more preferably 300-400 °C. The hydrogen brittleness of stainless is suppressed in this range, and the passivated film which contains close chromium oxide having an excellent degassing characteristic as a main component is obtained.

The surface roughness of the passivated film manufactured as described above is extremely smooth, and for example, when the above-mentioned passivated film formation treatment is performed after finishing into 0.05-0.1 μm by the electrolytic polishing, and further the hydrogen gas treatment is performed, then the passivated film having a surface roughness of not more than 0.01 μm is obtained.

(Annealing treatment)

Annealing treatment is further performed in inert gas after the hydrogen gas treatment, thereby the chromium oxide concentration in the outermost surface of the thermally oxidized passivated film is much increased, and stainless steel having the passivated film with much more excellent corrosion resistance is obtained. The annealing is preferably performed at 200-500 °C for 1-10 hours, and by performing the annealing under a condition within this range, the surface state of the thermally oxidized passivated film becomes smoother, the chromium oxide concentration in the outermost surface is much increased, and the corrosion resistance is much improved. As the inert gas to be used for the annealing treatment, for example, Ar, He, N_2 and the like are used.

(Passivating treatment for welded portions)

It has been found that when the stainless steel, in which the passivated film formation treatment is performed in the oxidizable atmospheric gas after performing the electrolytic polishing treatment of the surface of the stainless steel, and successively the iron oxide on the surface is reduced and removed by hydrogen gas to form the passivated film, or the stainless steel, in which the above-mentioned high temperature baking is performed in the inert gas atmosphere after performing the electrolytic polishing of the surface of the stainless steel so as to form the passivated film, is welded, the surface of welded portions is coated with a passivated film containing a larger amount of Fe oxide than one before the welding (Fig. 4).

Thus, a passivated film containing much Cr oxide can be formed at the welded portions by heating the welded portions after the welding and again performing the high temperature baking (300-600 °C x 1-10 hours) in the inert gas atmosphere, or by performing the passivated film formation treatment in the oxidizable atmospheric gas and successively reducing and removing iron oxide on the surface using hydrogen gas. Incidentally, the surface roughness of the passivated film at the welded portions formed by the method of ② becomes to have R_{max}: 0.1 μm or below.

(Stainless steel)

As described in the item of the background of the invention, no stainless steel having a passivated film with a surface roughness of R_{max}: 0.1 μm or below has hitherto existed. This results from the fact that in the prior art, even when the surface roughness is made minute by the electrolytic polishing, the surface becomes rough when the passivated film is formed thereafter by the thermal oxidation.

However, according to the above-mentioned method of the present invention, it is possible to easily manufacture the stainless steel having the passivated film with the surface roughness of R_{max}: 0.1 μm or below.

That is to say, one is the method in which the surface roughness is finished to be 0.05-0.1 μm by means of the electrolytic polishing, and the above-mentioned high temperature baking is performed. The fact that the passivated film is also formed by the high temperature baking is as described above, and the fact that the surface roughness during the electrolytic polishing is maintained also by the high temperature baking is also as described above. Therefore, when the high temperature baking is performed after the electrolytic polishing with respect to the surface roughness of 0.05-0.1 μm, the passivated film having the surface roughness of 0.05-0.1 μm is obtained. Incidentally, this passivated film is an extremely close passivated film in which the surface is extremely rich in chromium, Cr/Fe is of course 1 and more, and one having Cr/Fe of about 7 is also achieved (see Fig. 5).

Consequently, this stainless steel is extremely excellent in the degassing characteristic because R_{max} is 0.1 μm and more for the surface roughness, and it has the close passivated film.

Another method for obtaining the stainless steel having the passivated film with the surface roughness of R_{max}: not more than 0.1 μm is the method in which the surface of stainless steel is finished to have the surface roughness of R_{max}: 0.05-0.1 μm by means of the electrolytic polishing, and the above-mentioned hydrogen gas treatment is performed (the high temperature baking may be performed before the hydrogen gas treatment). Using this method, it is also possible to manufacture the stainless steel having the passivated film having the surface roughness of R_{max}:not more than 0.01 μm. Incidentally, Cr/Fe at the surface of the passivated one after the hydrogen gas treatment becomes larger than Cr/Fe in the base material (see Fig. 6, for example, Cr/Fe is 0.35 in Fig. 6 (a)), so that the stainless steel which is also excellent in the gas disengage characteristic and the corrosion resistance is obtained.

(Object stainless steel)

In addition, the stainless steel of the present invention is, for example, those of the Fe-Cr type and the Fe-Cr-Ni type. In addition, also with respect to the structure, any stainless steel of the ferrite type, the martensite type or the austenite type is available. Especially SUS 316 is preferable.

The passivated stainless steel manufactured according to the passivated film formation method of the present invention as described above exhibits extremely good degassing characteristics and corrosion resistance, which makes it possible to use as constituting materials for ultra-high vacuum apparatuses, ultra-high clean pressure-reducing apparatuses and the like.

(Gas-contacting parts and liquid-contacting parts)

The passivated stainless steel manufactured according to the passivated film formation method of the present invention as described above exhibits extremely good degassing characteristics and corrosion resistance, which is preferably used also for gas-contacting parts.

In addition, it has been found that when this stainless steel is allowed to contact with pure water, there is no elution of impurities from the stainless steel to pure water, and it is also excellent in corrosion resistance against corrosive chemical solutions. Therefore, the stainless steel according to the present invention can be preferably used also for liquid-contacting parts such as liquid supply tubes, liquid storing tanks and the like.

Next, concrete examples of the gas-contacting parts will be explained.

A system of a gas supply line for supplying gas from a gas bomb to a use point of the gas such as a film formation apparatus or the like generally has constitution as shown in Fig. 7. In Fig. 7, 100 is the gas cylinder, 101 is a gas cylinder valve, 102 is a regulator, 103 is a valve, 104 is an integrated branched valve, 105 is a mass flow controller, 106 is the film formation apparatus, 107 is a pipe arrangement, and 108 is a filter.

As the gas-contacting parts, for example, there are exemplified parts such as the gas cylinder valve, a pressure gauge, the regulator, the valve, the mass flow controller, the filter, the regulator and the like, or for example, a valve seat, a valve chamber, a valve main body, a diaphragm, a seal ring, a stem and the like constituting these parts.

As the cylinder valve, for example, one having a structure shown in Fig. 8 is exemplified (official gazette of Japanese Utility Model Application Laid-open No. HEI-1-178281-1989). In addition, those shown in Fig. 9 for the pressure gauge, in Fig. 10 for the regulator, in Fig. 11 for the valve and in Fig. 12 for the mass flow controller are exemplified as each of examples, respectively.

For example, in the case of the diaphragms exemplified in Fig. 8, Fig. 9 and Fig. 11, following effects are also provided. Preferably the diaphragm has its small surface roughness from a viewpoint of the sealing property. In addition, in order to give deflection, resiliency is required. Further, in order to ensure a good sealing property for a long time, an excellent fatigue resistance characteristic is required. However, in the present invention, R_{max} is not more than 0.1 μm for its surface roughness, so that the sealing property is extremely good. In addition, it is generally considered that metal having a passivated film is inferior in resiliency to metal having no passivated film, however, in the present invention, resiliency which is not different from that of stainless having no passivated film at all has been exhibited. Further, as a result of a fatigue test, a critical fatigue strength which is more excellent than that of stainless steel formed with a conventional passivated film has been exhibited. In addition, in the case of the stainless formed with the conventional passivated film, generation of small cracks was found on its surface, however, in the case of the stainless according to the present invention, generation of such cracks was not found.

In addition, the good sealing property is also required in the case of the valves such as the cylinder valve for gas cylinders and the like, however, the valve of the present invention has a better sealing property than a valve having a conventional passivated film on the gas-contacting surface, in which the leak amount is remarkably reduced, and it has become possible to supply gas of ultra-high purity.

Further, when a pure water supply tube was manufactured using the stainless steel according to the present invention, ultra-pure water having a resistivity of about 18 MΩ•cm was supplied in the tube, and the resistivity at an outlet was measured, then the resistivity value scarcely changed.

In addition, when the stainless steel according to the present invention was immersed in an HCl solution, and the surface was observed by microphotograph, then no corrosion on the surface was found.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a graph showing degassing characteristics of oxidized passivated stainless tubes manufactured by various methods, wherein

(a): a thermally oxidized passivated film manufactured by a conventional method,

(b): an oxidized passivated film manufactured by a wet method,

(c): a thermally oxidized passivated film manufactured in a ultra-high purity oxidizable atmosphere of a moisture content of not more than 10 ppb,

(d): a thermally oxidized passivated film of Embodiment 1,

(e): a thermally oxidized passivated film of Embodiment 2,

(f): a thermally oxidized passivated film of Embodiment 3,

(g): a thermally oxidized passivated film of Embodiment 4, and

(h): a thermally oxidized passivated film of Embodiment 5.

Fig. 2 is scanning type electron microphotographs showing inner surface states of a stainless tube before and after an electrolytic polishing treatment.

Fig. 3 is scanning type electron microphotographs showing inner surface states of a stainless tube after electrolytic polishing.

Fig. 4 is a graph showing concentration profiles in the depth direction by XPS after welding.

Fig. 5 is a graph showing concentration profiles in the depth direction by XPS of the electrolytic polishing surface after baking in an Ar gas atmosphere.

Fig. 6 is graphs showing concentration profiles in the depth direction by XPS of the thermally oxidized passivated film surface after the hydrogen reduction treatment.

(a): treatment time 10 minutes, (b): treatment time 30 minutes.

Fig. 7 is a figure of concept showing a system of a gas supply line.

Fig. 8 is a cross-sectional view of a bomb valve according to one embodiment of the present invention.

Fig. 9 is a cross-sectional view of a pressure gauge according to one embodiment of the present invention.

Fig. 10 is a cross-sectional view of a regulator according to one embodiment of the present invention.

Fig. 11 is a cross-sectional view of a valve according to one embodiment of the present invention.

Fig. 12 is a cross-sectional view of a mass flow controller according to one embodiment of the present invention.

Fig. 13 is scanning type electron microphotographs showing inner surface states of stainless tubes after baking in an Ar gas atmosphere.

Fig. 14a is scanning type electron microphotographs showing surface states of a thermally oxidized passivated film after the hydrogen reduction treatment for 10 minutes.

Fig. 14b is scanning type electron microphotographs showing surface states of a thermally oxidized passivated film after the hydrogen reduction treatment for 30 minutes.

Fig. 15 is a graph showing concentration profiles in the depth direction by XPS of the thermally oxidized passivated film surface after the Ar annealing treatment.

(a): annealing temperature: 375 °C,
(b): annealing temperature: 400 °C,
(c): annealing temperature: 425 °C,
(d): annealing temperature: 450 °C,
(e): annealing temperature: 475 °C,
(f): annealing temperature: 500 °C.

Fig. 16 is a graph showing the relation between the system leak amount and the impurity concentration in the atmospheric gas for various gas flow rates in a conventional apparatus.

Fig. 17 is a graph showing concentration profiles in the depth direction by XPS of the thermally oxidized passivated film surface manufactured by a conventional thermal oxidation method.

Fig. 18 is scanning type electron microphotographs showing the surface state of a thermally oxidized passivated film manufactured by a conventional method.

(Description of the References)

100:	cylinder, 101: gas cylinder valve, 102: pressure gauge / regulator
103:	valve, 104: branched valve, 105: mass flow controller,
106:	film formation apparatus, 107: pipe arrangement,
108:	filter.

BEST MODE FOR CARRYING OUT THE INVENTION

Embodiments of the present invention will be explained hereinafter.

(Embodiment 1)

A SUS 316L stainless tube having a length of 2 m and a diameter of 3/8" was subjected to electrolytic polishing, and the surface was made into a specular face in which the maximum value of difference in irregularity (R_{max}) was 0.05 μm in within a circumference having a radius of 5 μm. As shown in Fig. 3, this surface state is a smooth face in which the crystal grain boundary is observed.

Next, this stainless tube was washed by the same method as a washing process of wafers, namely in the order of ammonia/hydrogen peroxide/water ($NH_4OH:H_2O_2:H_2O = 1:4:20$, 90 °C), hot water washing (90 °C) and ultra-pure water, which was dried with isopropyl alcohol.

This stainless tube was installed in an oxidation furnace, Ar gas was allowed to flow at 1 l/min, purging was performed at an ordinary temperature for 1 hour, thereafter the temperature was raised to 450-550 °C, and a baking treatment was performed for 10 hours. Inner surface states of the stainless after the thermal treatment at various temperatures are shown in Fig. 13. As clarified from Fig. 13, even after the thermal treatment for a long time at a high temperature, the specular face after the electrolytic polishing was maintained for the stainless surface. That is to say, R_{max}: 0.05 μm was maintained. In addition, a result of measurement by XPS of the inner surface of the stainless tube after the baking at 500 °C is shown in Fig. 5. Owing to the above-mentioned baking treatment, chromium atoms increased at the surface side, while iron atoms inversely decreased, and the chromium/iron composition ratio was inverted with respect to the inside of the bulk.

In Fig. 5, the place at which the line of Fe intersects with the line of O is a boundary between the bulk (base material) and the passivated film, and the film thickness of the passivated film shown in Fig. 5 is about 30 Å. In this passivated film, chromium oxide is more than iron oxide in one of about 22 Å from the surface (left end of the graph in Fig. 5).

Subsequently the inside of the oxidation furnace was lowered to 400 °C, thereafter the Ar gas was replaced by a mixed gas of Ar and O_2 containing 100 ppb of moisture ($Ar/O_2 = 4:1$), and the inner surface of the stainless tube was subjected to an oxidation treatment. A surface state after the oxidation is approximately the same surface state as one shown in the electron microphotographs in Fig. 18, in which a large number of cracks and pin holes were observed on the film surface.

Next, the oxidizable gas was purged by Ar gas, Ar gas containing 1 ppm of H_2 was introduced into the stainless tube, and a hydrogen reduction treatment of the oxidized film was performed at 400 °C for 10 minutes or 30 minutes. Surface states after the treatment are shown in Fig. 14 (a) (in the case of 10 minutes) and Fig. 14 (b) (in the case of 30 minutes), respectively. Fig. 14 (a) indicates the case in which the hydrogen gas treatment time was 10 minutes, and Fig. 14 (b) indicates the case in which the hydrogen gas treatment time was 30 minutes. As shown by Fig. 14, the cracks and pin holes having existed after the oxidation treatment were not observed on the surface of the passivated film subjected to the hydrogen reduction treatment (hydrogen gas treatment), and the smooth surface state was provided. On the other hand, as shown in Fig. 6, a high concentration of chromium oxide existed in the passivated film, and the chromium atomic ratio with respect to iron became by far larger than that in the base material. Incidentally, the thickness of the passivated films shown in Fig. 6 (a) and Fig. 6 (b) was about 60 Å.

As a result of measurement of the surface roughness of this passivated film, there was given R_{max}: 0.01 μm.

According to the above-mentioned facts, it is considered that the layer of iron oxide in which a large number of pin holes and cracks existed was removed, the close layer containing a large amount of chromium oxide appeared, and the surface became clean and flat.

In addition, it was found that the hydrogen reduction treatment time scarcely affected the surface state of the passivated film and the concentration profile in the depth direction, and the reduction reaction was completed for about 10 minutes.

Next, with respect to the stainless tube having been subjected to the above-mentioned passivating treatment, an evaluation test for the degassing characteristic was performed. After the stainless tube was left for 1 week in a clean room at a relative humidity of 50 % and a temperature of 20 °C, Ar gas was allowed to flow in a flow rate of 1.2 l/min, and the moisture amount contained in the Ar gas was measured at the outlet of the tube using APIMS (atmospheric pressure ionization mass spectrometer). A result is shown in (d) in Fig. 1. The moisture amount in the Ar gas decreased to 10 ppb 20 minutes after the gas application, which became not more than 3 ppb as the background level after 30 minutes.

As compared with a oxidized passivated film manufactured by the conventional method shown in Fig. 1 (a), the degassing characteristic was greatly improved, and it has been shown that the oxidized passivated film stainless steel manufactured according to the present embodiment can be applied to ultra-high vacuum apparatuses and ultra-high clean pressure-reduced apparatuses.

(Embodiment 2)

The baking treatment in the Ar atmosphere was omitted in embodiment 1, and other things were the same as those in embodiment 1, whereby an oxidized passivated stainless tube was manufactured in the same manner as embodiment 1, and its degassing characteristic was evaluated. A result is shown in (e) in Fig. 1.

As clarified from Fig. 1, the moisture amount became 3 ppb about 40 minutes after the gas application, in which the degassing characteristic was inferior to that of the oxidized passivated film of embodiment 1, however, it was greatly improved as compared with the conventional oxidized passivated film.

(Embodiment 3)

An oxidized passivated film was formed on the inner surface of a stainless tube, in which the temperature of the hydrogen reduction treatment was 600 °C, and other treatment conditions were the same as those in embodiment 1, and the same evaluation was performed.

A result is shown in (f) in Fig. 1. Roughness was observed a little on the surface of the passivated film manufactured herein, and the degassing characteristic was also inferior to those of embodiments 1 and 2, however, the moisture content decreased to 3 ppb about 70 minutes after the gas application, which was clearly improved as compared with the conventional example.

(Embodiment 4)

An oxidized passivated film was formed on the inner surface of a stainless tube, in which the hydrogen reduction treatment gas was Ar gas containing 20 % hydrogen, and other conditions were the same as those in embodiment 1, and the same evaluation was performed.

A result is shown in (g) in Fig. 1. Roughness was observed a little on the surface of the passivated film, and the degassing characteristic was also inferior to those of embodiments 1 and 2, however, the moisture content decreased to 3 ppb about 70 minutes after the gas application, which was clearly improved as compared with the conventional example.

(Embodiment 5)

An oxidized passivated stainless tube was manufactured, in which the oxidizable atmosphere was a ultra-high purity atmosphere of a moisture concentration of 5 ppb, and other treatment conditions were the same as those in embodiment 1, and its degassing characteristics was evaluated. The results is as in (h) in Fig. 1. The moisture amount in the Ar gas became not more than 3 ppb as the background level 10 minutes after the gas application, and it was found that even in the case of the film at the highest level at the present circumstance, the degassing characteristic was improved by the treatment according to the present embodiment.

(Embodiment 6)

The hydrogen reduction treatment was performed in the same manner as embodiment 1, and then the annealing treatment was further performed at various temperatures for 10 hours in Ar gas. Concentration profiles in the depth direction by XPS at the surface of the thermally oxidized passivated films are shown in Fig. 15 (a) to Fig. 15 (f).

As clarified from Fig. 8, owing to the Ar annealing, the concentration of chromium having high corrosion resistance increased at the outermost surface layer. Moreover, it was found that the chromium concentration increased more and more in accordance with the increase in the treatment temperature, and the concentrations of chromium and iron became inverted at not less than 475 °C. Incidentally, the thickness of the passivated films shown in Fig. 8 (a) to Fig. 8 (f) was about 70 Å.

In addition, with respect to the oxidized passivated film of the present embodiment, the corrosion resistance was improved owing to the increase in the chromium concentration at the outermost surface, and extremely good corrosion resistance was exhibited against a strongly corrosive solution of 36 % HCl.

INDUSTRIAL APPLICABILITY

According to the present invention, it becomes possible to form the passivated film which is extremely excellent in the degassing characteristic and the corrosion resistance, and it becomes possible to supply the oxidized passivated stainless steel which is applicable to ultra-high vacuum, ultra-high clean pressure-reduced apparatuses and the like.

Claims

1. A method for forming stainless steel passivated films wherein the surface of stainless steel is subjected to an electrolytic polishing treatment, thereafter an oxidation treatment is performed in oxidizable atmospheric gas, and subsequently iron oxide on the surface is reduced and removed using hydrogen gas.

2. The method for forming stainless steel oxidized passivated films according to claim 1 wherein a heat treatment is performed in an inert gas atmosphere at 300-600 °C after said electrolytic polishing treatment and before said oxidized film formation.

3. The method for forming stainless steel oxidized passivated films according to claim 1 or 2 wherein the hydrogen concentration in the gas atmosphere is 0.1 ppm to 10 % in said hydrogen gas treatment.

4. The method for forming stainless steel oxidized passivated film according to any one of claims 1 through 3 wherein the treatment temperature is 200-500 °C in said hydrogen gas treatment.

5. The method for forming stainless steel oxidized passivated films according to any one of claims 1 through 4 wherein an annealing treatment is performed in inert gas after said hydrogen gas treatment.

6. The method for forming stainless steel oxidized passivated films according to claim 5 wherein the condition for said inert gas annealing treatment is at 200-500 °C for 1-10 hours.

7. The method for forming stainless steel oxidized passivated films according to claim 6 wherein the condition for said inert gas annealing treatment is at not less than 475 °C.

8. A method for forming stainless steel passivated films wherein stainless steel, in which the surface is subjected to an electrolytic polishing treatment, thereafter an oxidation treatment is performed in oxidizable atmospheric gas, and subsequently iron oxide on the surface is reduced and removed using hydrogen gas, is

mutually welded, next an oxidation treatment is performed in oxidizable atmospheric gas while heating a welded portion, and subsequently iron oxide on the surface is reduced and removed using hydrogen gas.

9. Stainless steel wherein it has a passivated film in which R_{max} is not more than 0.1 μm for the surface roughness.

10. The stainless steel according to claim 9 wherein it has the passivated film in which R_{max} is not more than 0.01 μm for the surface roughness.

11. The stainless steel according to claim 9 or claim 10 wherein Cr/Fe (atomic ratio, followings are the same) of the surface of the passivated film is larger than Cr/Fe of the base material portion.

12. The stainless steel according to claim 9 wherein Cr/Fe of the surface of the passivated film is not less than 1.

13. A gas-contacting part and a liquid-contacting part having on the surface a stainless steel passivated film formed such that the surface of stainless steel is subjected to an electrolytic polishing treatment, thereafter an oxidation treatment is performed in oxidizable atmospheric gas, and subsequently iron oxide on the surface is reduced and removed using hydrogen gas.

14. The gas-contacting part and the liquid-contacting part having at least on the gas-contacting surface and the liquid-contacting surface the stainless steel passivated film according to claim 13 wherein a heat treatment is performed in an inert gas atmosphere at 300-600 °C after said electrolytic polishing treatment and before said oxidized film formation.

15. The gas-contacting part and the liquid-contacting part having on the surface the stainless steel passivated film according to claim 13 or 14 wherein the hydrogen concentration in the gas atmosphere is 0.1 ppm to 10 % in said hydrogen gas treatment.

16. The gas-contacting part and the liquid-contacting part having on the surface the stainless steel passivated film according to any one of claims 13 to 15 wherein the treatment temperature is 200-500 °C in said hydrogen gas treatment.

17. The gas-contacting part and the liquid-contacting part having on the surface the stainless steel passivated film according to any one of claims 13 through 16 wherein an annealing treatment is performed in inert gas after said hydrogen gas treatment.

18. The gas-contacting part and the liquid-contacting part having on the surface the stainless steel passivated film according to claim 17 wherein the condition for said inert gas annealing treatment is at 200-500 °C for 1-10 hours.

19. The gas-contacting part and the liquid-contacting part having on the surface the stainless steel passivated film according to claim 18 wherein the condition for said inert gas annealing treatment is at not less than 475 °C.

20. A gas-contacting part and a liquid-contacting part having on the surface a stainless steel passivated film wherein they have the passivated film in which R_{max} is not more than 0.1 μm for the surface roughness.

21. The gas-contacting part and the liquid-contacting part having on the surface the stainless steel passivated film according to claim 20 wherein they have the passivated film in which R_{max} is not more than 0.01 μm for the surface roughness.

22. The gas-contacting part and the liquid-contacting part having on the surface the stainless steel passivated film according to claim 9 or claim 21 wherein Cr/Fe (atomic ratio, followings are the same) of the surface of the passivated film is larger than Cr/Fe of the base material portion.

23. The gas-contacting part and the liquid-contacting part having on the surface the stainless steel passivated film according to claim 20 wherein Cr/Fe of the surface of the passivated film is not less than 1.

24. The gas-contacting part and the liquid-contacting part having on the surface the stainless steel passivated film according to any one of claims 20 through 23 wherein said gas-contacting part and said liquid-contacting part are a diaphragm in a regulator or a valve.

25. The gas-contacting part and the liquid-contacting part according to any one of claims 20 through 23 wherein said gas-contacting part is a cylinder valve of a gas cylinder, and the cylinder valve is such a cylinder valve of the gas cylinder in which a gas inlet is allowed to communicate with a gas outlet through a gas inlet passage, a valve chamber for gas supply and a gas outlet passage in a valve main body of the cylinder valve,

a valve body for gas supply is provided in the valve chamber for gas supply, and the valve body for gas supply is constituted to be capable of opening and closing operation with respect to a valve seat of the valve chamber for gas supply by a valve for gas supply operating unit, which is such a cylinder valve of the gas cylinder in which

a valve chamber for protection is allowed to intervene in the gas outlet passage in the valve main body of the cylinder valve, a valve body for protection is provided at the valve chamber for protection, and the valve body for protection is constituted to be capable of opening and closing operation with respect to a valve seat of the valve chamber for protection by a valve for protection operating unit.

FIG 1

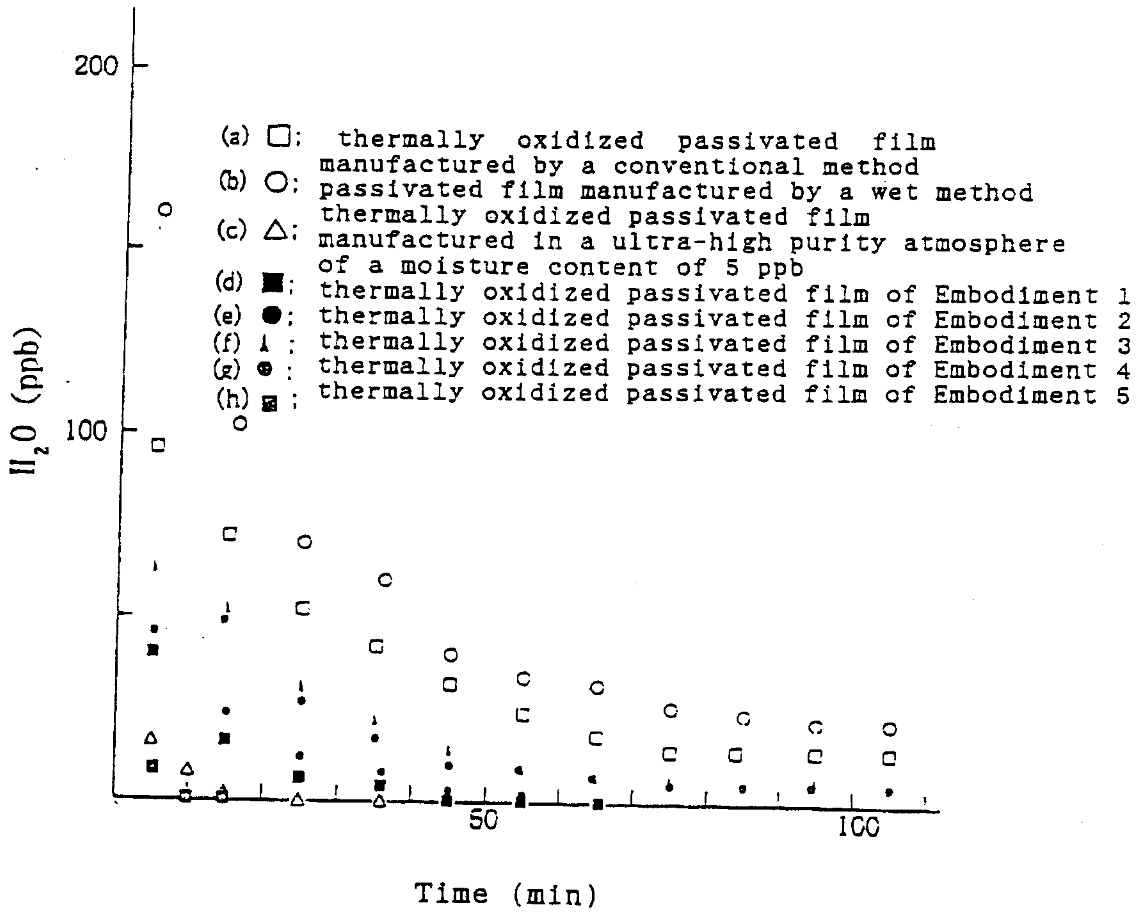
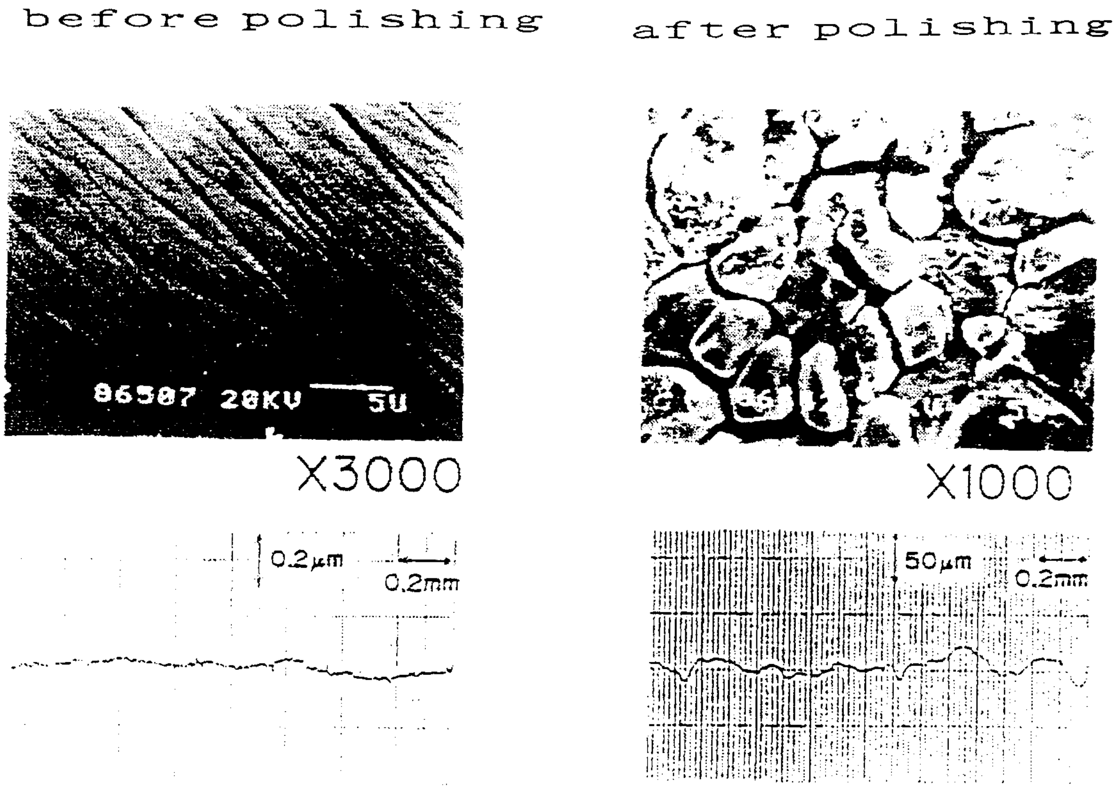

200
100
H_2O (ppb)
50
100
Time (min)
(a) □: thermally oxidized passivated film manufactured by a conventional method
(b) ○: passivated film manufactured by a wet method
(c) △: thermally oxidized passivated film manufactured in a ultra-high purity atmosphere of a moisture content of 5 ppb
(d) ■: thermally oxidized passivated film of Embodiment 1
(e) ●: thermally oxidized passivated film of Embodiment 2
(f) ⅰ : thermally oxidized passivated film of Embodiment 3
(g) ⊛ : thermally oxidized passivated film of Embodiment 4
(h) ▨ : thermally oxidized passivated film of Embodiment 5

FIG2

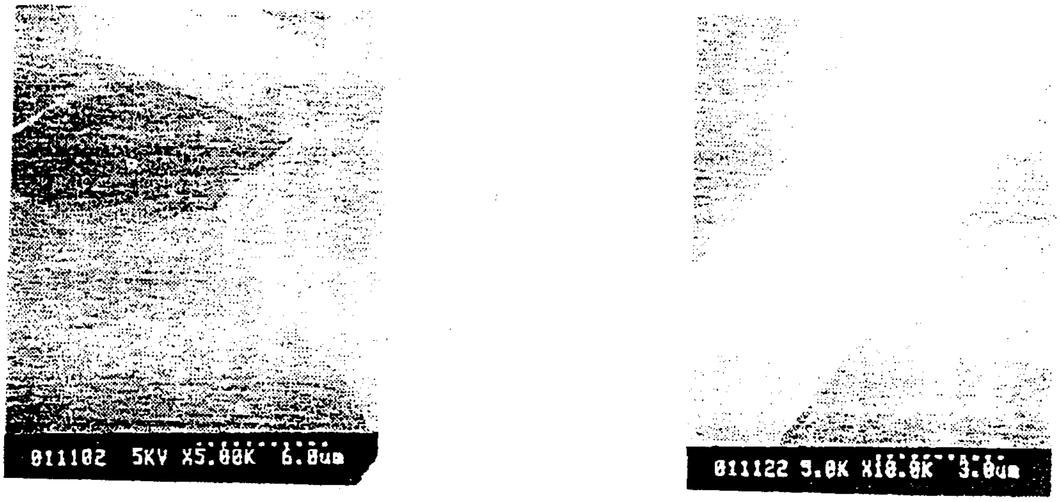

before polishing
after polishing
86507 20KV 5U
X3000
X1000
0.2μm
0.2mm
50μm
0.2mm

(a)

(b)

FIG3

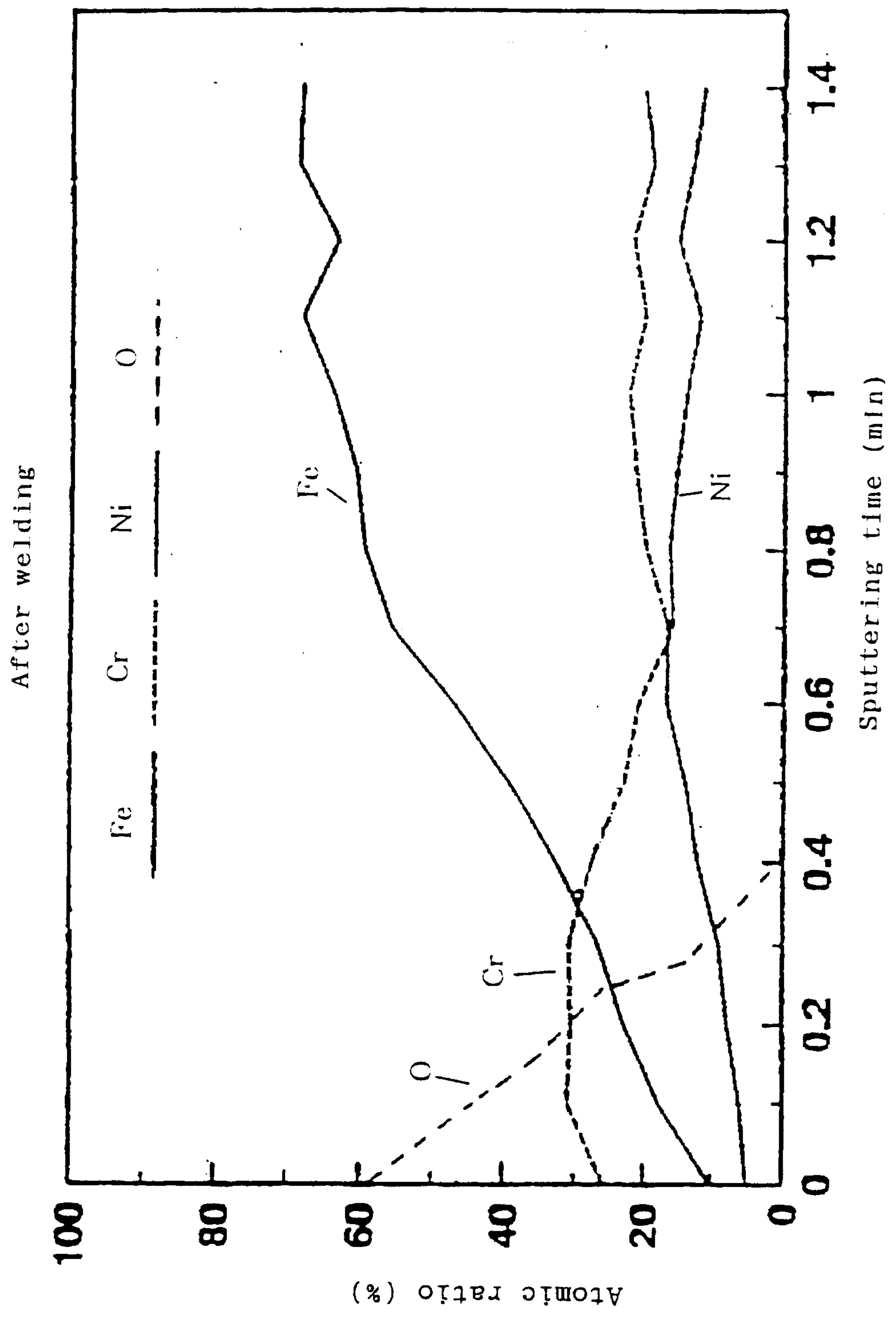
Conventional electrolytically polished tube surface



×5000

×10000

FIG 4


After welding
Fe
Cr
Ni
O
Fe
Cr
O
Ni
100
80
60
40
20
0
Atomic ratio (%)
0
0.2
0.4
0.6
0.8
1
1.2
1.4
Sputtering time (min)

F I G 5

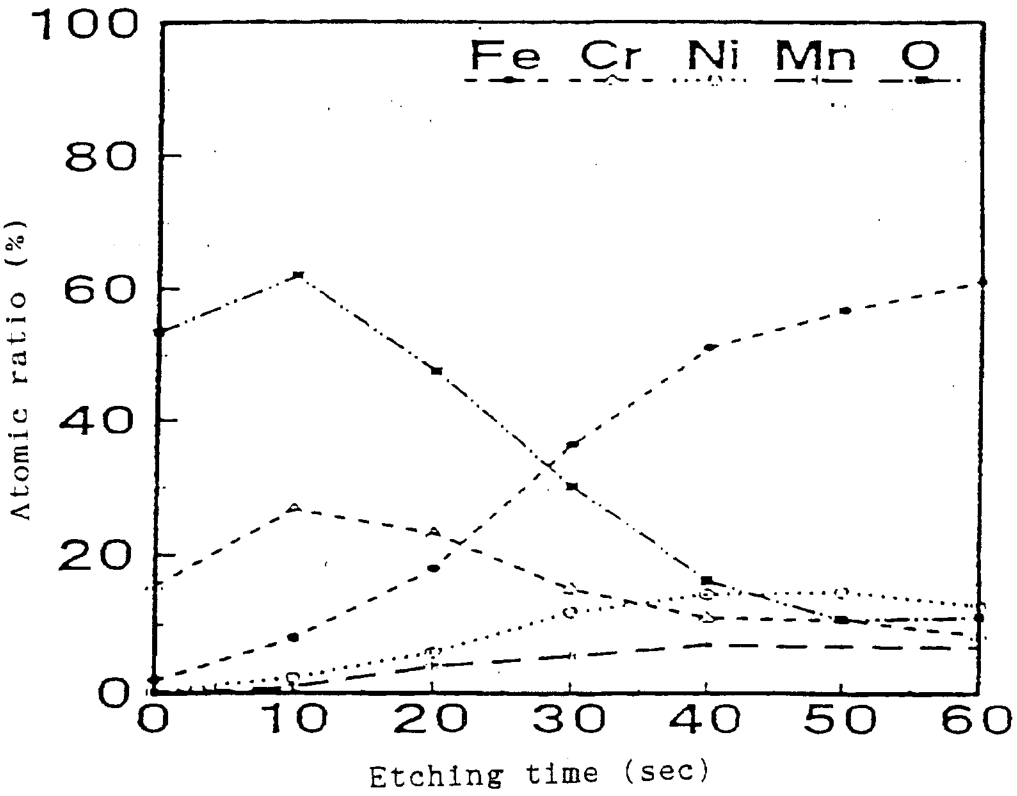
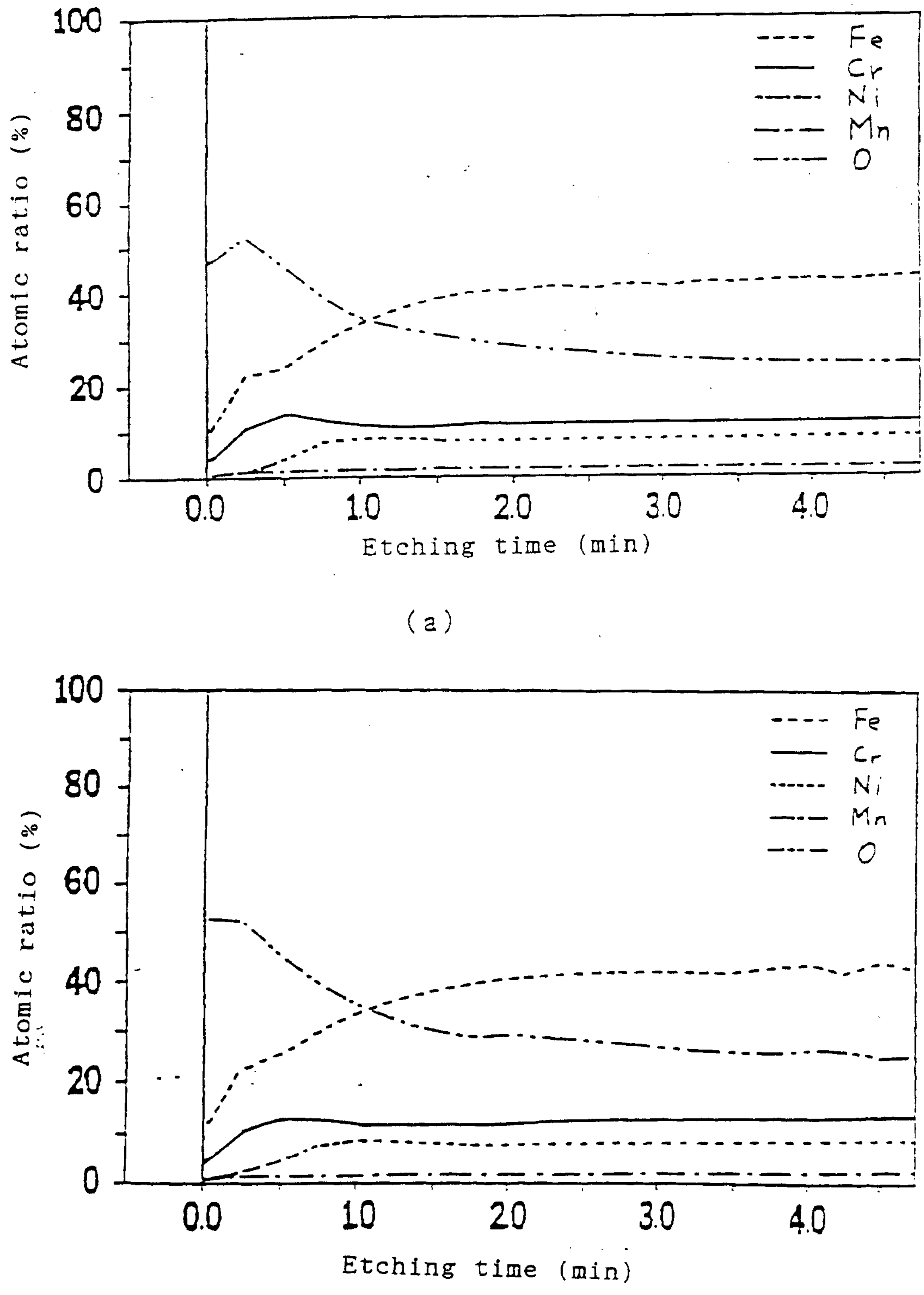

Fe
Cr
Ni
Mn
O
100
80
60
40
20
0
0
10
20
30
40
50
60
Atomic ratio (%)
Etching time (sec)

FIG 6


100
80
60
40
20
0
Atomic ratio (%)
0.0
1.0
2.0
3.0
4.0
Etching time (min)
Fe
Cr
Ni
Mn
O
100
80
60
40
20
0
Atomic ratio (%)
0.0
1.0
2.0
3.0
4.0
Etching time (min)
Fe
Cr
Ni
Mn
O

(a)

(b)

F I G 7

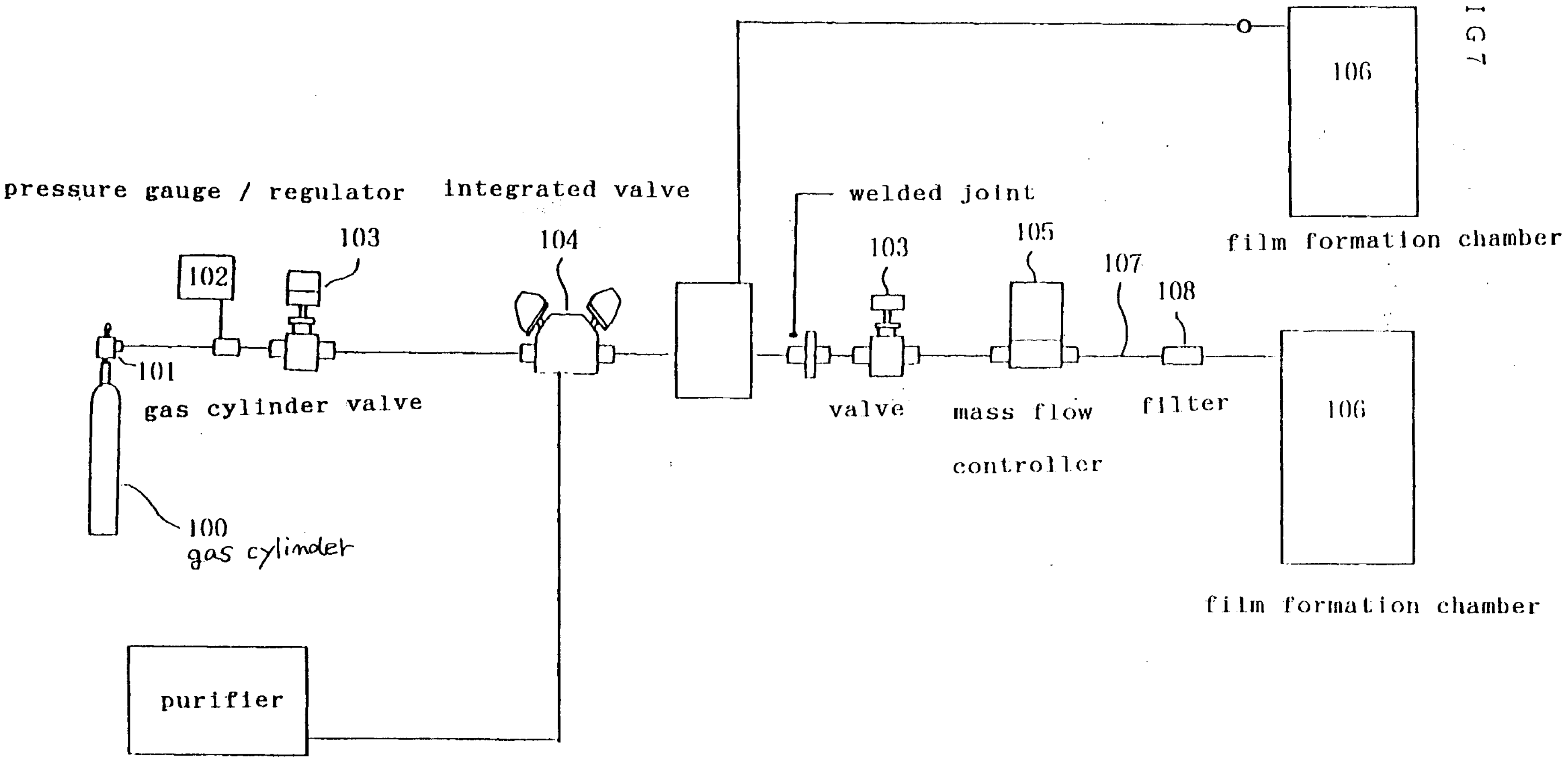
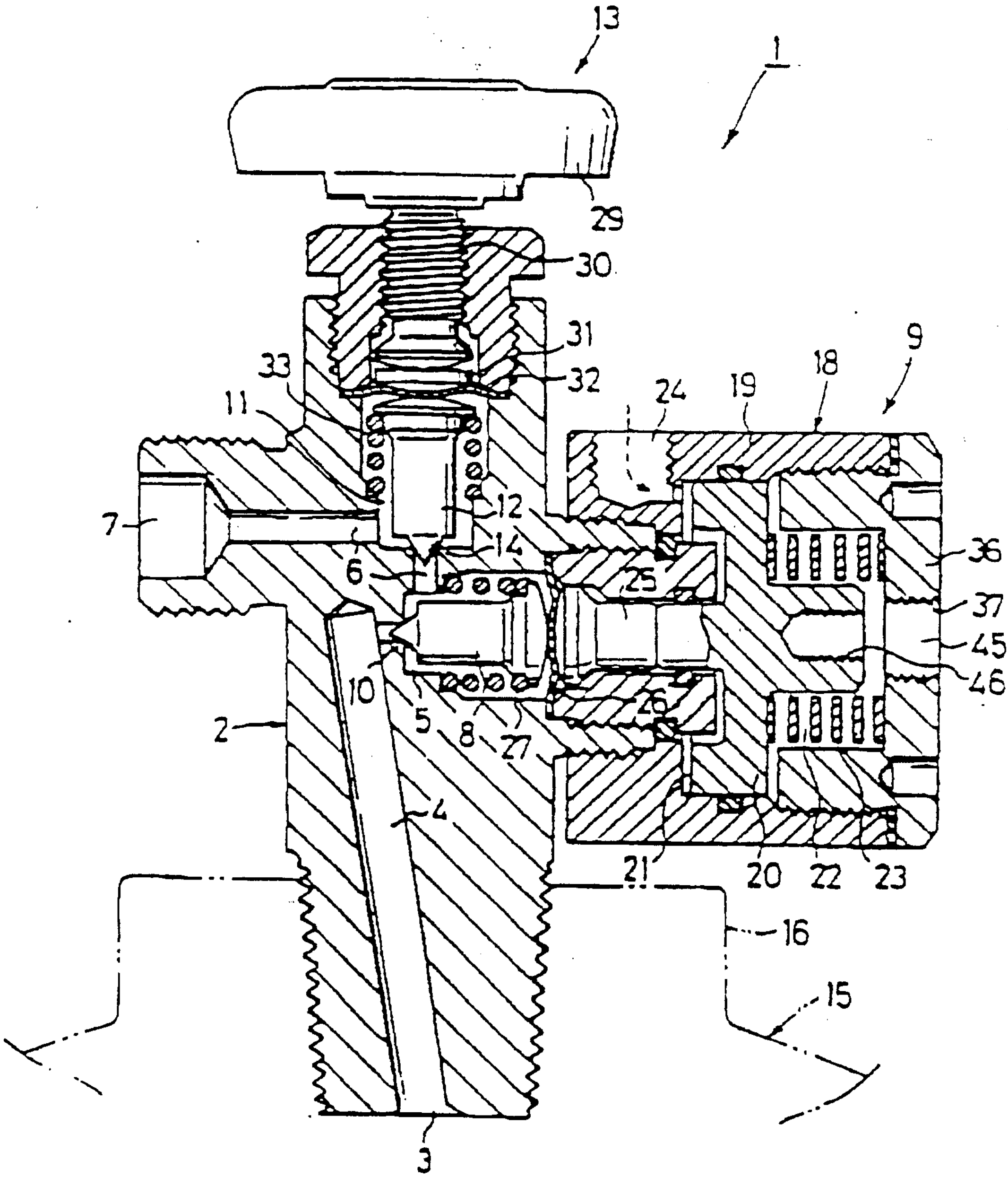

106
film formation chamber
106
film formation chamber
pressure gauge / regulator
integrated valve
welded joint
102
103
104
103
105
107
108
101
gas cylinder valve
valve
mass flow
controller
filter
100
gas cylinder
purifier

FIG8



1: cylinder valve 2: valve main body 3: gas inlet
4: gas inlet passage 5: valve chamber for gas supply
6: gas outlet passage 7: gas outlet
8: valve body for gas supply
9: valve for gas supply operating unit
10: valve seat 11: valve chamber for protection
12: valve body for protection
13: valve for protection operating unit
14; valve seat 26: diaphragm

F I G 9

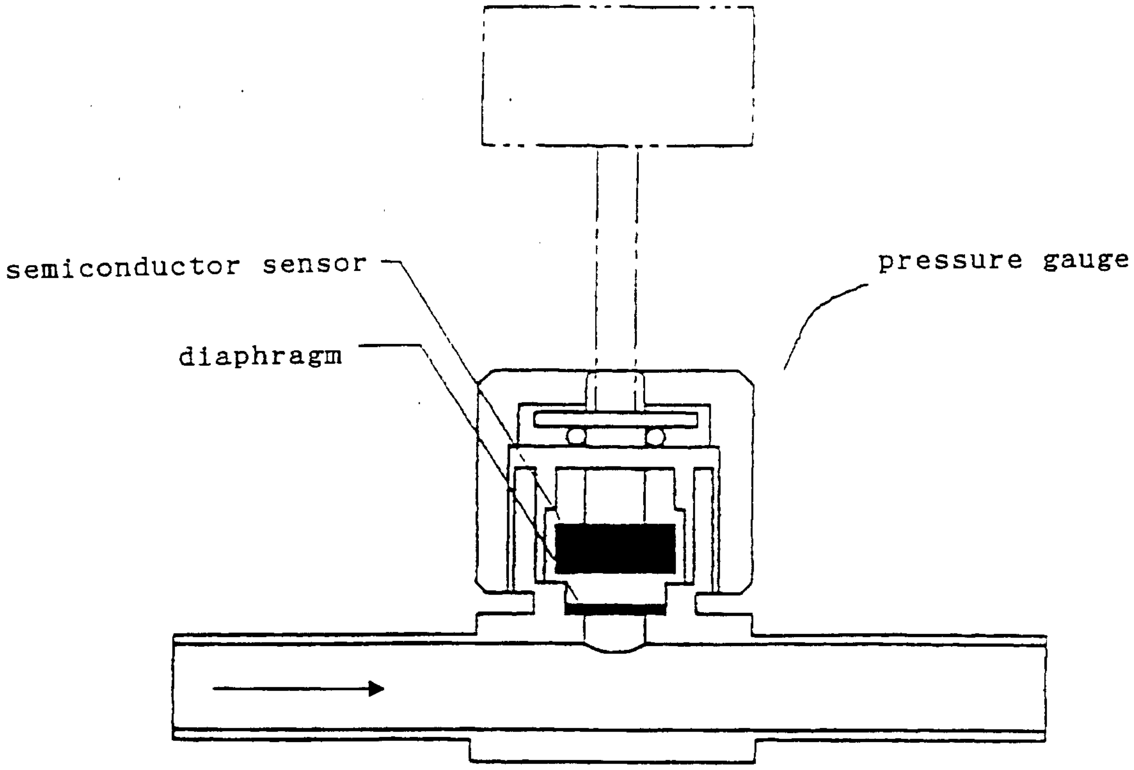


FIG10

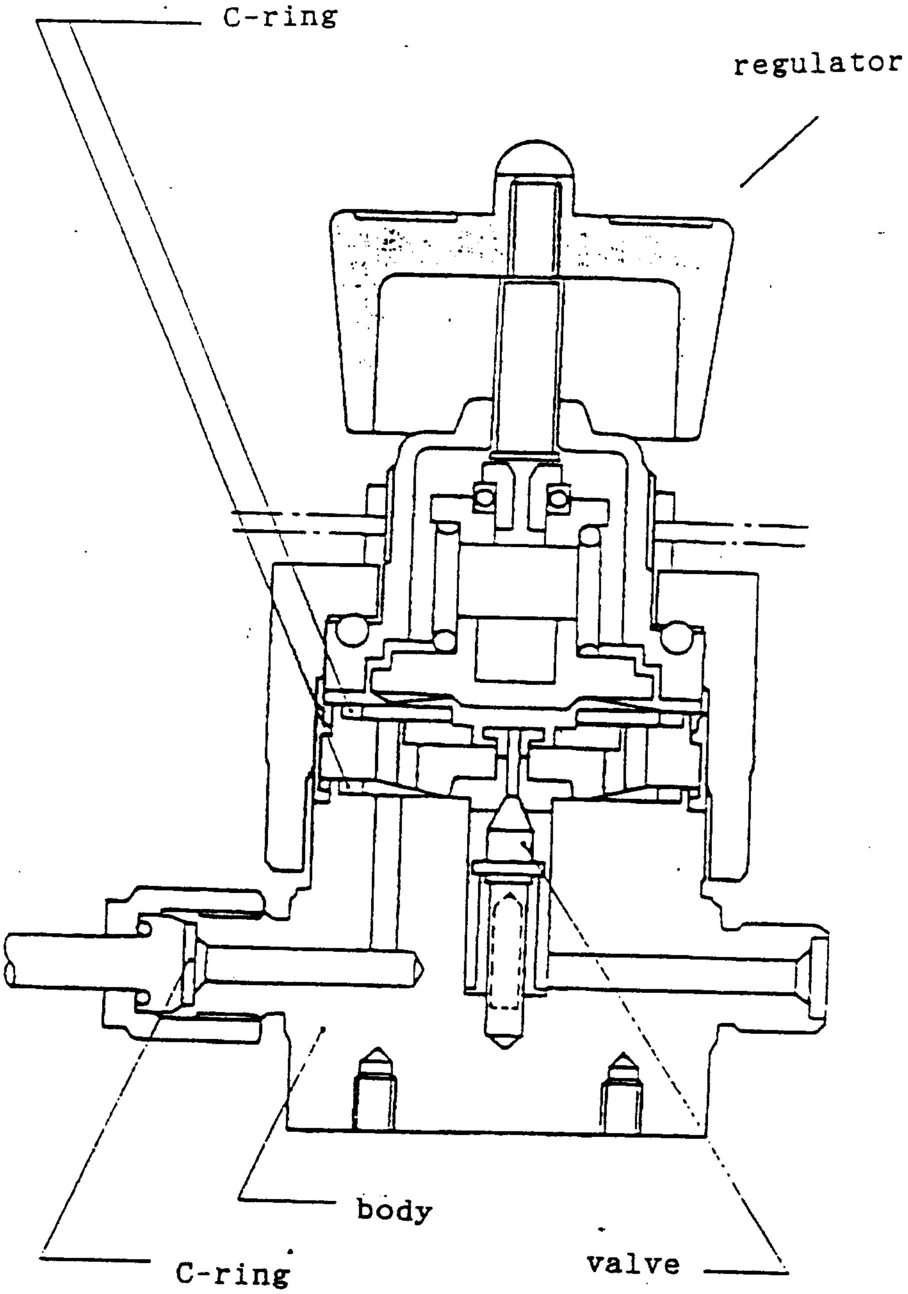


FIG 11

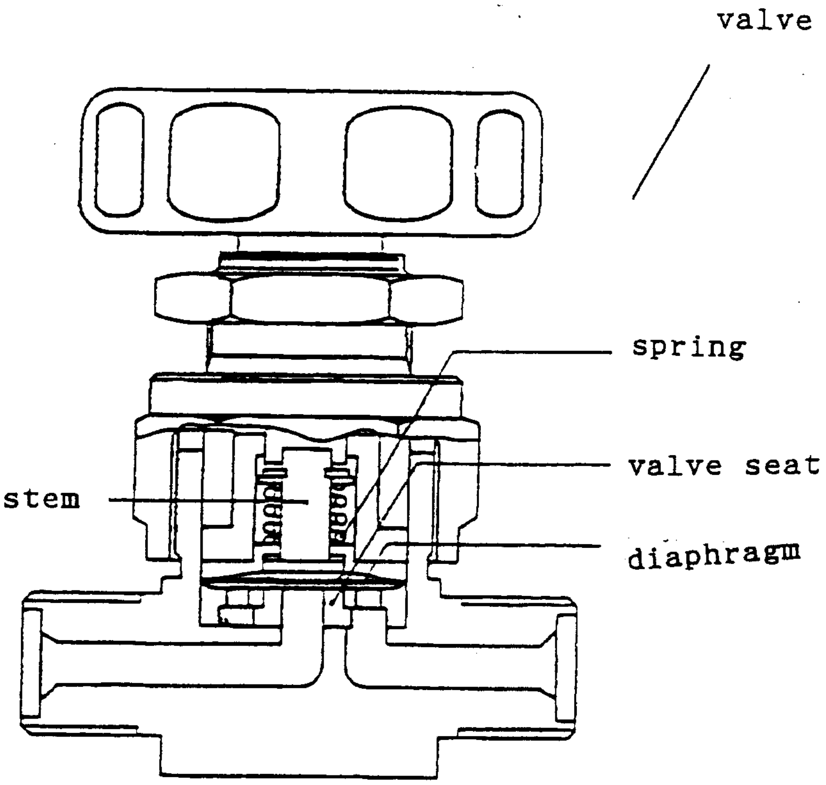


FIG12

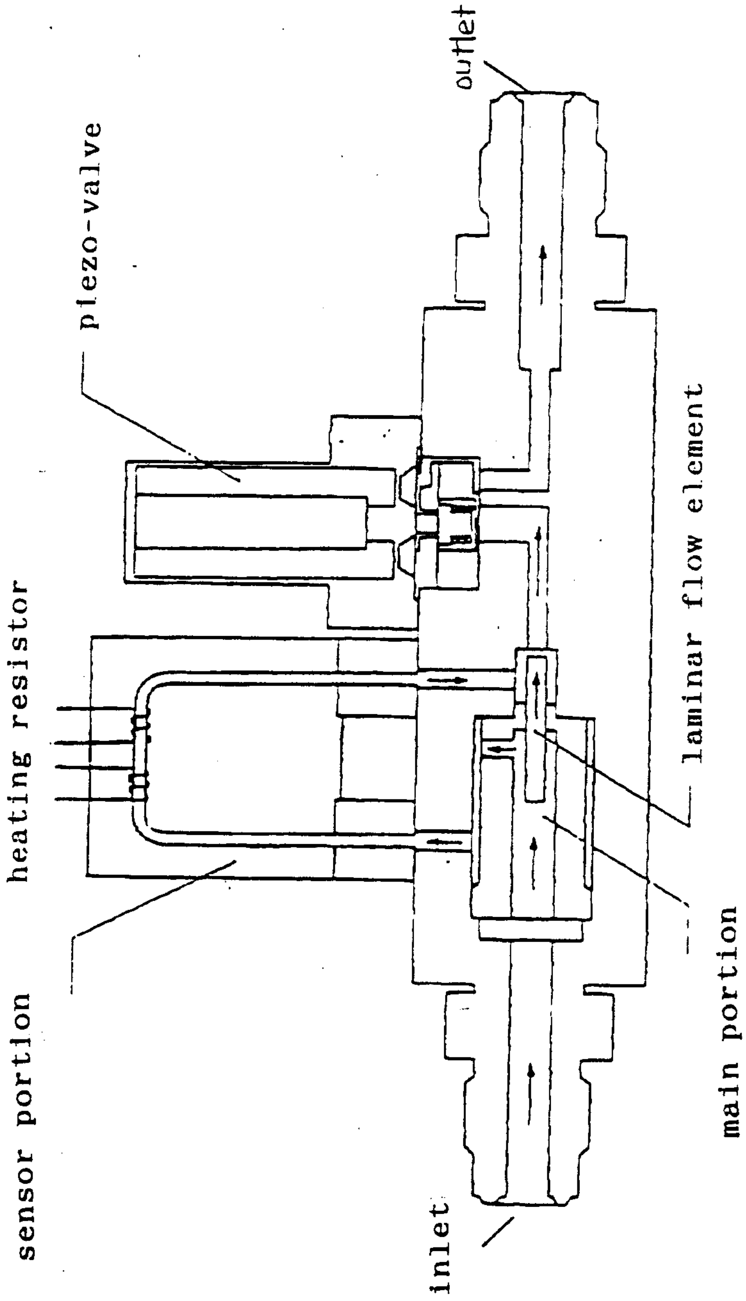
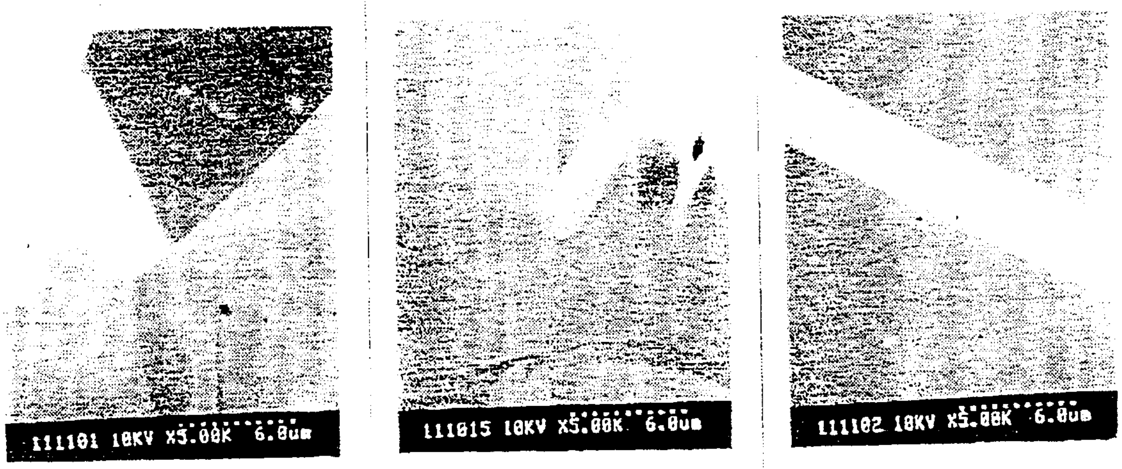

sensor portion
heating resistor
piezo-valve
outlet
laminar flow element
main portion
inlet

FIG13

Stainless surface resulting from Ar baking only (x 5000)

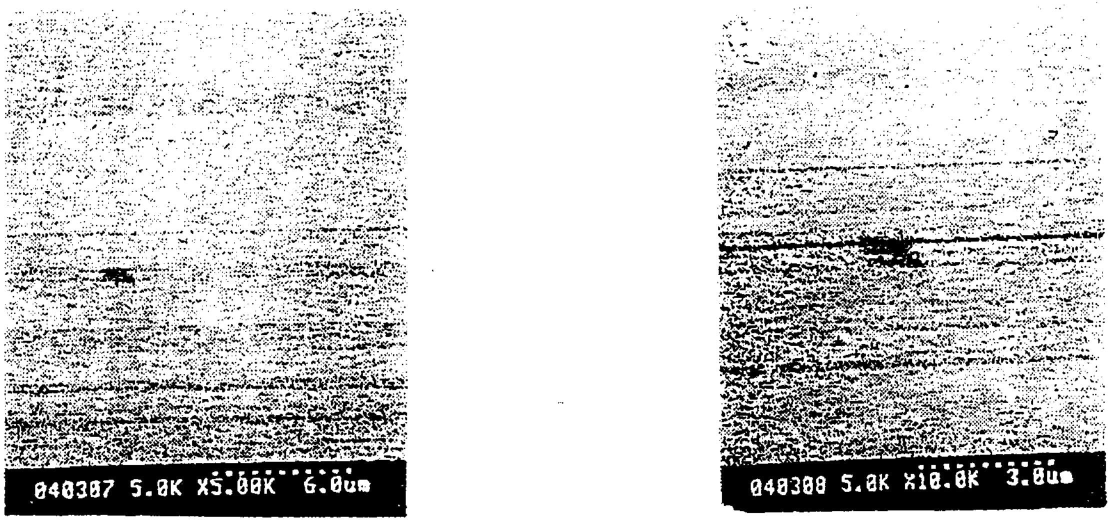


450°C 500°C 550°C

FIG14

(a)

Reduction in H_2 at 400 °C for 10 minutes



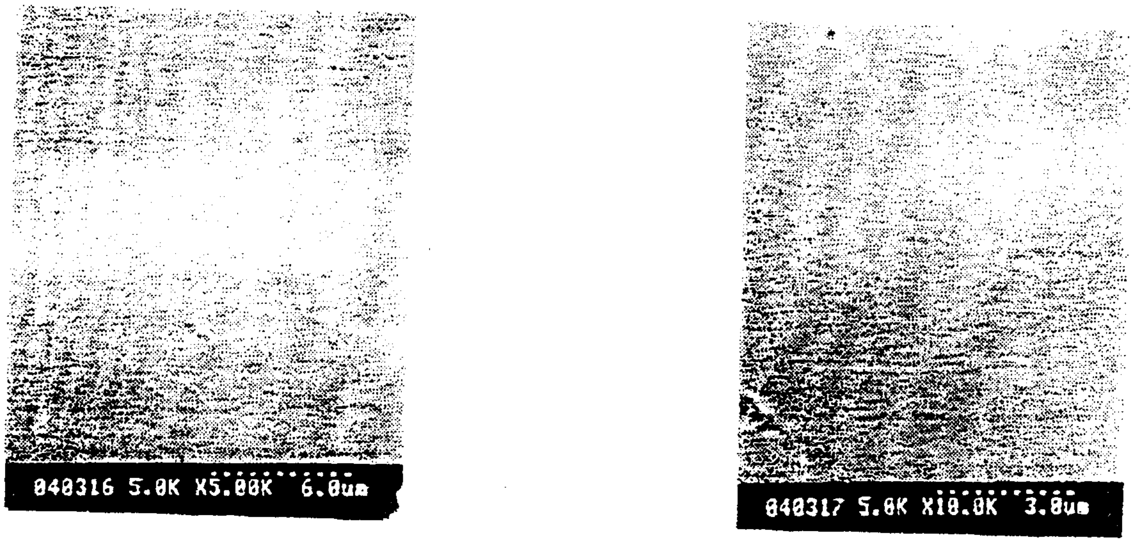
×5000

×10000

FIG14

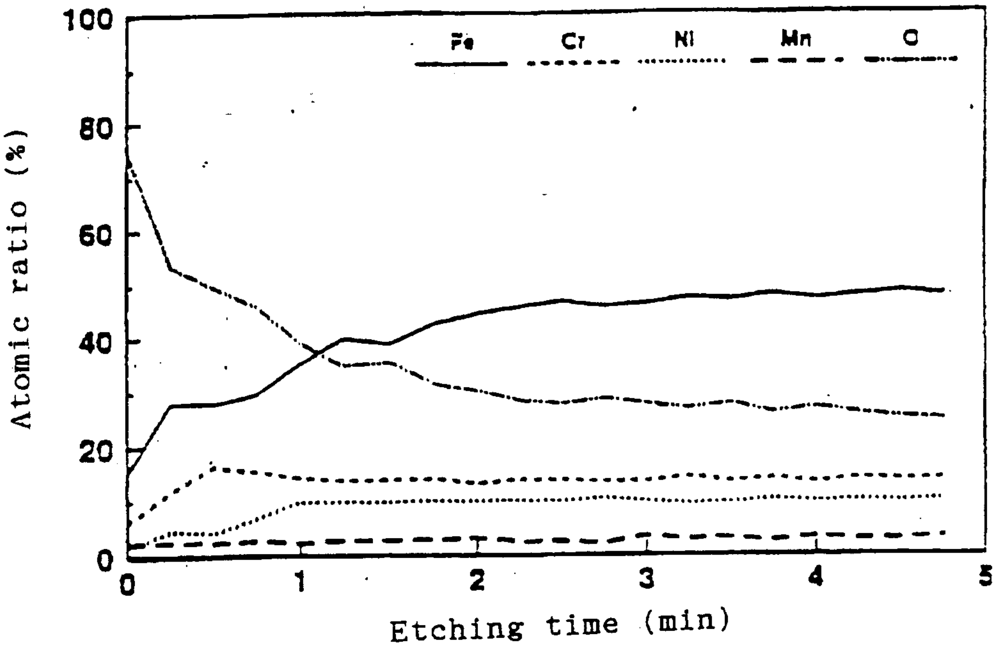
(b)

Reduction in H_2 at 400 °C
for 30 minutes

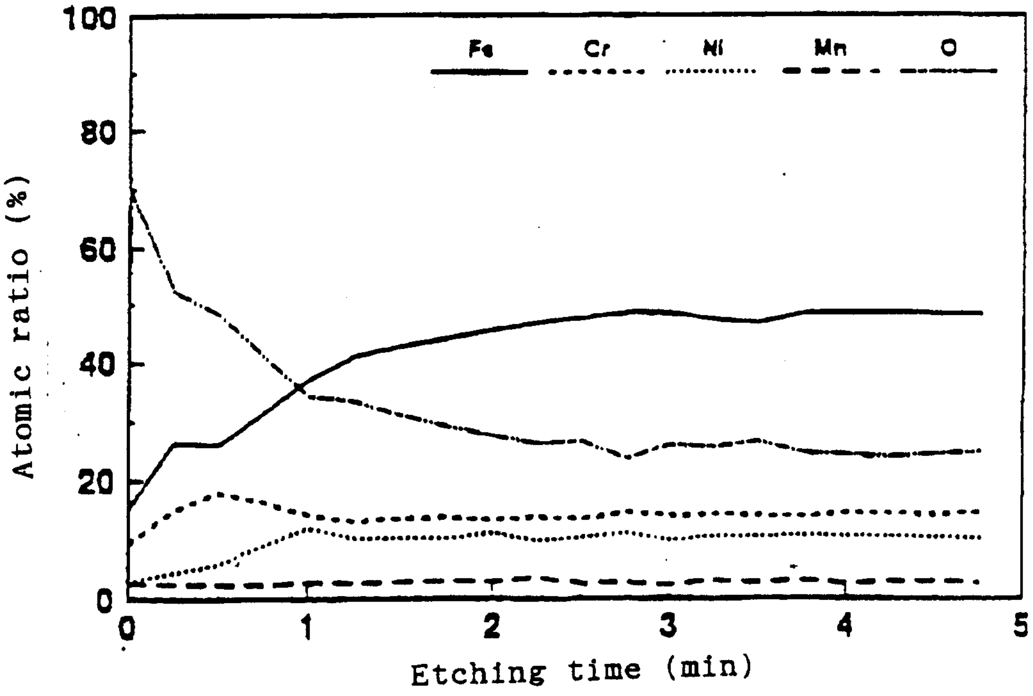


×5000 ×10000

FIG15

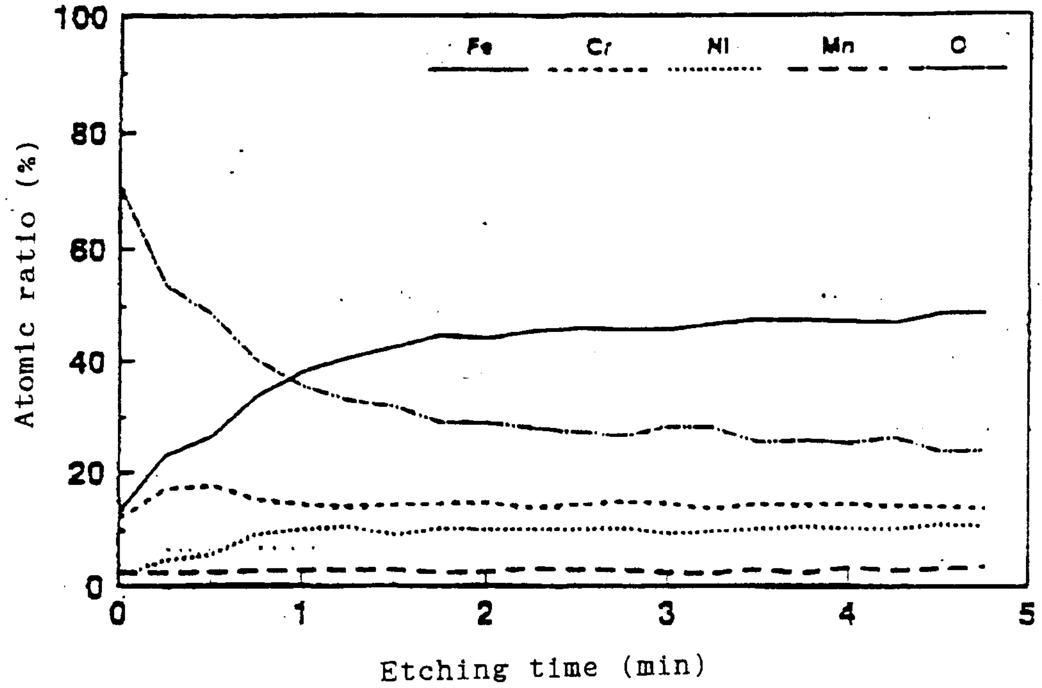

100
80
60
40
20
0
Atomic ratio (%)
0
1
2
3
4
5
Etching time (min)
Fe
Cr
Ni
Mn
O

(a)

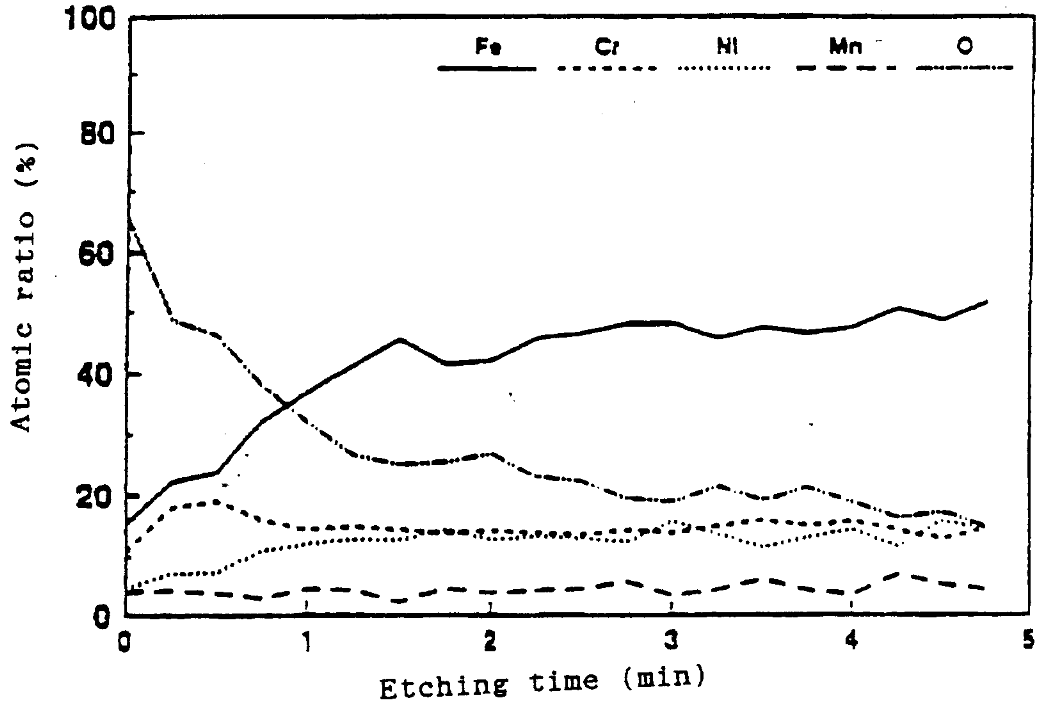

100
80
60
40
20
0
Atomic ratio (%)
0
1
2
3
4
5
Etching time (min)
Fe
Cr
Ni
Mn
O

(b)

FIG15

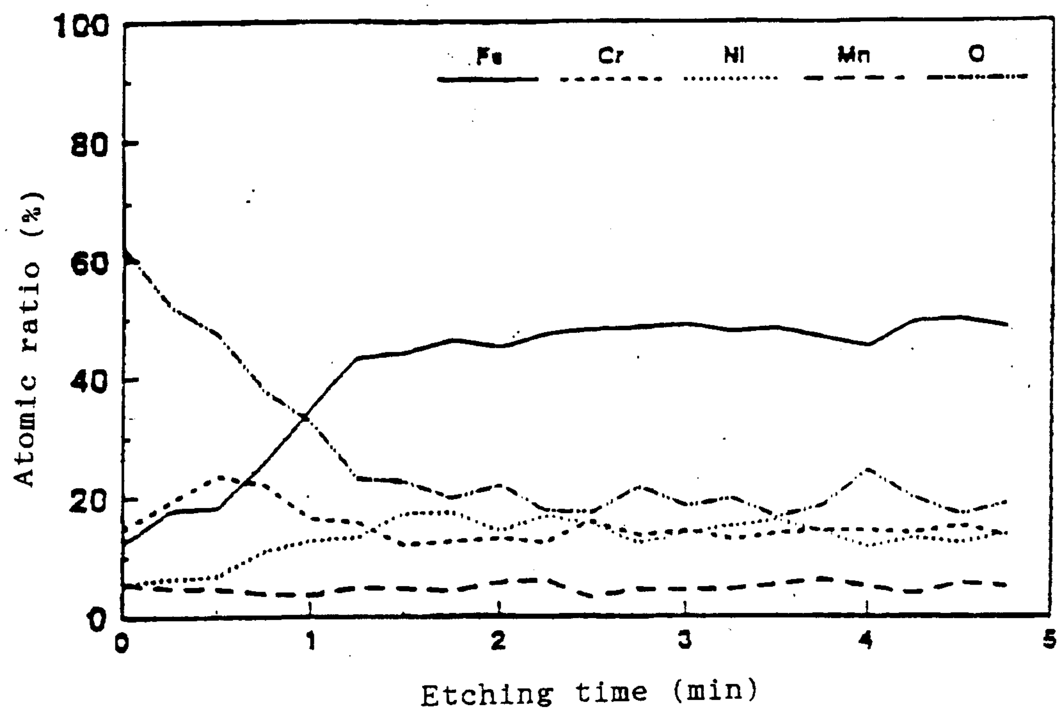

Fe
Cr
Ni
Mn
O
Atomic ratio (%)
100
80
60
40
20
0
0
1
2
3
4
5
Etching time (min)

(c)

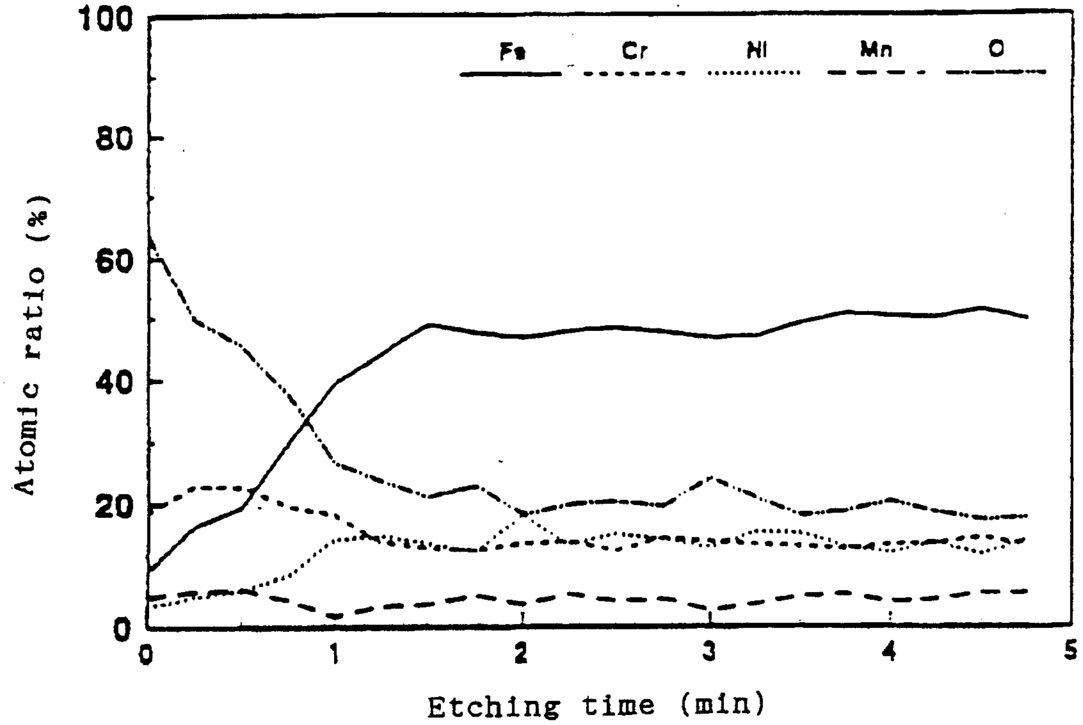

Fe
Cr
Ni
Mn
O
Atomic ratio (%)
100
80
60
40
20
0
0
1
2
3
4
5
Etching time (min)

(d)

FIG15


100
80
60
40
20
0
Atomic ratio (%)
0
1
2
3
4
5
Etching time (min)
Fe
Cr
Ni
Mn
O

(e)


100
80
60
40
20
0
Atomic ratio (%)
0
1
2
3
4
5
Etching time (min)
Fe
Cr
Ni
Mn
O

(f)

FIG16

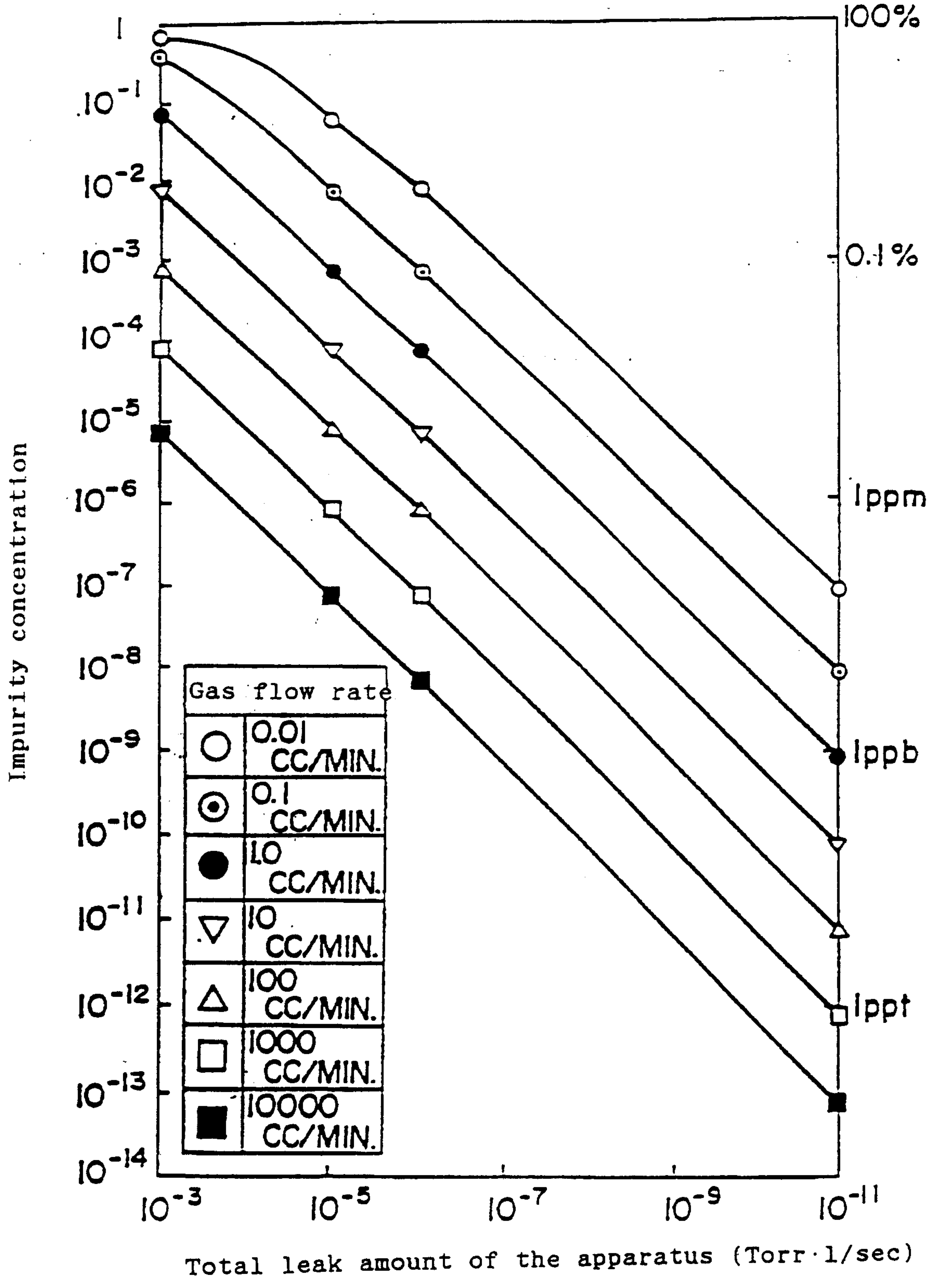

1
10⁻¹
10⁻²
10⁻³
10⁻⁴
10⁻⁵
10⁻⁶
10⁻⁷
10⁻⁸
10⁻⁹
10⁻¹⁰
10⁻¹¹
10⁻¹²
10⁻¹³
10⁻¹⁴
100%
0.1%
1ppm
1ppb
1ppt
Impurity concentration
Gas flow rate
○ 0.01 CC/MIN.
⊙ 0.1 CC/MIN.
● 1.0 CC/MIN.
▽ 10 CC/MIN.
△ 100 CC/MIN.
□ 1000 CC/MIN.
■ 10000 CC/MIN.
10⁻³
10⁻⁵
10⁻⁷
10⁻⁹
10⁻¹¹
Total leak amount of the apparatus (Torr·l/sec)

FIG 17

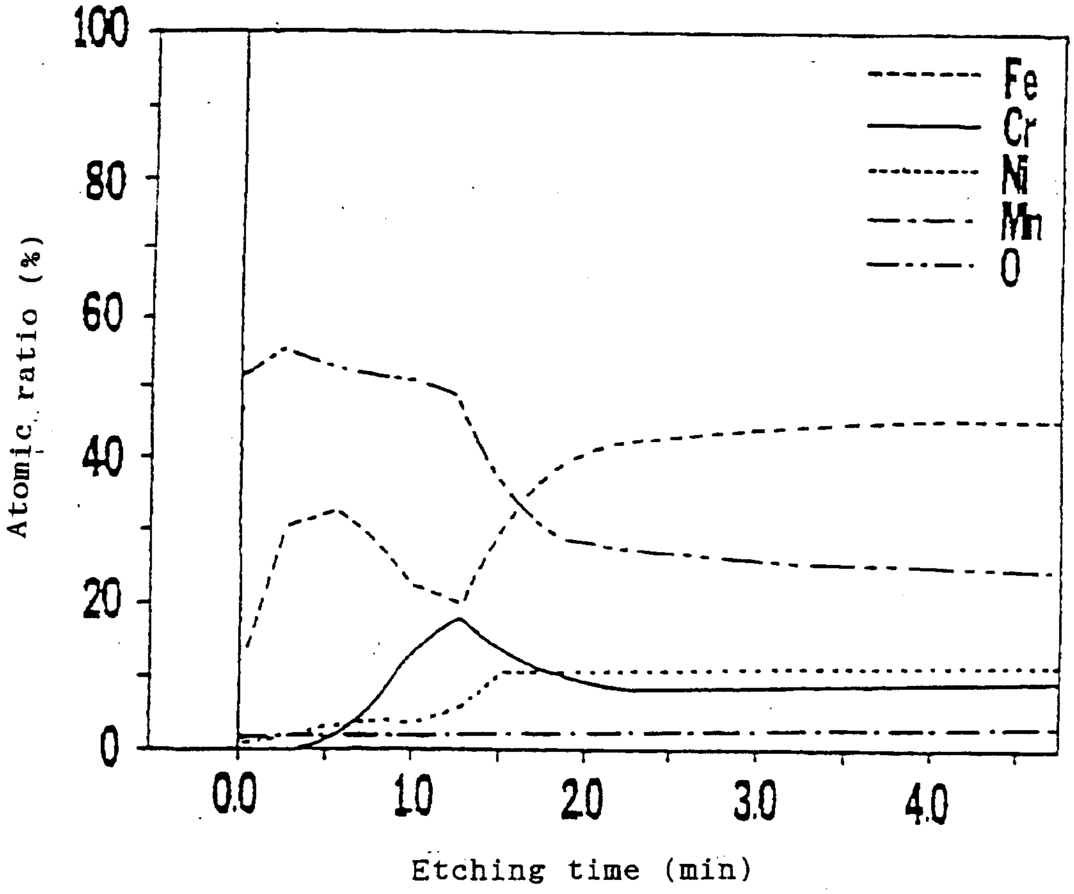

100
80
60
40
20
0
Atomic ratio (%)
0.0
1.0
2.0
3.0
4.0
Etching time (min)
Fe
Cr
Ni
Mn
O

FIG18

Stainless surface applied with the oxidization passivating treatment

×5000

×10000

INTERNATIONAL SEARCH REPORT

International Application No PCT/JP92/00699

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [6]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int. Cl^5 C23C8/14, 8/80, C21D6/00

II. FIELDS SEARCHED

Minimum Documentation Searched [7]

Classification System	Classification Symbols
IPC	C23C8/10-8/18, 8/80, C21D6/00

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [8]

Jitsuyo Shinan Koho	1919 - 1992
Kokai Jitsuyo Shinan Koho	1971 - 1992

III. DOCUMENTS CONSIDERED TO BE RELEVANT [9]

Category *	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No. [13]
A	JP, A, 64-31956 (Tadahiro Omi, Kobe Steel, Ltd.), February 2, 1989 (02. 02. 89), Line 3, upper left column to line 9, lower left column, page 2 (Family: none)	1-25
A	JP, A, 2-43353 (Tadahiro Omi, Osaka Sanso Kogyo K.K.), February 13, 1990 (13. 02. 90), Line 19, lower left column, page 7 to line 1, upper left column, page 8, line 17, upper right column to line 7, lower left column, page 8 (Family: none)	1-25

* Special categories of cited documents: [10]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"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

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

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IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
August 25, 1992 (25. 08. 92)	September 8, 1992 (08. 09. 92)
International Searching Authority	**Signature of Authorized Officer**
Japanese Patent Office	