The present invention relates to a method of protecting metallic apparatus from the corrosive effects of high-temperature, high-pressure NH₃ gas by fabricating the apparatus from a stainless steel of austenitic structure comprising 5 to 12% chromium, 17 to 40% nickel, 0.5 to 4% copper or niobium, the balance being mainly iron.

The object of this invention is to offer an economical solution to the problem of the corrosion, chiefly through nitriding, of the metallic materials of apparatus when exposed to high-temperature, high-pressure NH₃ gas, said solution being in the adoption of a cheap, easily workable stainless steel with high anti-corrosive properties.

It has long been known that various irons and steels, when exposed to NH₃ gas at over 400°C, will suffer serious corrosion through nitriding.

It has been observed that this nitriding corrosion of iron and steel by such high temperature NH₃ gas will make considerable progress in both a synthetic NH₃ atmosphere with an NH₃ concentration of a mere 2 to 20% and a normal pressure NH₃ gas, as encountered in the practice of producing a nitriding steel.

In the very early stage of nitriding irons and steels, the surface nitriding layer represents a very hard, stiff film of close texture, but as the nitriding process progresses, this layer transforms itself steadily into a fragile scale, finally falling off the body of metal.

Therefore, it is very important in the process of NH₃ synthesis to choose an anti-nitriding material with low vulnerability to nitriding corrosion for the metallic members of apparatus coming into contact with high-temperature NH₃ gas or for the members of the nitriding box to be employed in the production of nitriding steel, and much research has been devoted to this subject.

This research has shown that anti-nitriding property would be improved by increasing the nickel content of steel. Thus, Hastelloy, Inconel, etc., have come to be recommended as excellent materials for such purposes.

These high nickel alloys, however, are regarded as uneconomic because of extremely high expense and poor workability or weldability, although they may excel in resistance to nitriding.

As a matter of fact, 5 to 20% chromium stainless steels, e.g., 18 Cr-8 Ni, steel for NH₃ synthesis, and 25 Cr-20 Ni steel for nitriding box have more often been used, in spite of the corrosive reaction which results.

In the course of research on the use of a high-temperature, high-pressure NH₃ gas of heavy concentration under pressures of 50 to 350 kg/cm² and at temperatures of 350 to 550°C, the present inventors have found that the nitriding corrosion in such high-temperature, high-pressure NH₃ gas of high concentration is much more intense than in high-pressure NH₃ gas of low concentration or in normal pressure NH₃ gas of high concentration, and have realized that chemical production processes involving such high-temperature, high-pressure NH₃ gas of high concentration will be hamstrung unless some new grade of stainless steel with excellent anti-nitriding property could be developed.

Even at 350°C. a relatively intense nitriding corrosion is in evidence in an NH₃ gas of over 50% concentration with a pressure of more than 50 kg/cm², and at a pure NH₃ gas with 100 kg/cm², 400°C, the nitriding corrosion of AISI 316, i.e., 18 Cr-14 Ni-2 Mo stainless steel, will amount to 1 mm/year.

Such high nickel alloys as Hastelloy and Inconel are highly anti-nitriding to such high-temperature, high-pressure NH₃ gas of heavy concentration, but as stated above, they have been found impractical because of high cost and poor workability.

Particularly, it is extremely difficult or even impossible to fabricate stainless tubes or high pressure vessels from these alloys.

The present inventors have succeeded in perfecting the present invention as the result of meticulous investigations of the relation between Cr and Ni contents and the resistance to nitriding of stainless steels having a far smaller Ni content than said high nickel alloys, with a view to developing a stainless steel which is strongly anti-nitriding and at the same time cheap and easy to work.

If a stainless steel of austenitic structure comprising 5 to 12% chrome, 17 to 40% nickel and the rest mainly iron is employed to construct apparatus which is to be exposed to an NH₃ gas of over 10% concentration with pressure 50 to 350 kg/cm², temperature 350 to 550°C, such steel will successfully resist corrosion by such high-temperature, high-pressure NH₃ gas.

With over 12% chromium content, according to Tamman's law of active limit the effect of chromium begins to prevail and the resistance to nitriding remarkably deteriorates. On the contrary, if the chromium content drops below 5%, this resistance is also seriously lowered for some unknown reason. Meanwhile, in the range from 5 to 12% chromium there is a general tendency for the resistance to nitriding to improve with a decreasing chromium content.

An increase in the percentage of nickel above 40% does not result in any substantial improvement in the resistance to nitriding, but the cost will increase and the utility will become poor. This will make the production of seamless tubes, high pressure vessels particularly difficult.

At less than 17% nickel, the resistance to nitriding will seriously deteriorate.

It is widely believed that any increase in the nickel content will increase the resistance to nitriding but this does not always hold. Take, for example, the case of Incoloy. This 20% chromium 35% Ni alloy is found to be remarkably inferior in resistance to nitriding, even poorer in this respect than 18 Cr-8 Ni stainless steels.

On the other hand, Hastelloy or Inconel, containing more than 75% nickel, is found superior in its resistance to nitriding, in spite of a chrome content as high as 15%, but is expensive and hard to work.

An extremely significant discovery made by the present inventors in connection with the improvement in resistance to nitriding is the fact that a stainless steel with high resistance to nitriding may be found among low chromium stainless steels with 5 to 12% chromium, even though they contain less than 40% nickel.

Of equal importance is the fact that a combination of appropriate contents of chromium and nickel must be selected within the limits of 5 to 12% chrome and 17 to 40% nickel, so that the structure of the stainless steel may be kept austenitic.
Even if the chrome content is held within 5 to 12% and the nickel within 17 to 40%, the resistance to nitriding of a non-austenitic stainless steel will be very poor.

The stainless steel as proposed in the page 1 invention is equally or more resistant than 18 Cr-8 Ni to hydrogen embrittlement. No susceptibility to hydrogen embrittlement is observed as tested by the sectional structure of the test piece used in the test of Example 1.

Further, in the test with NH₃ gas under a pressure of 50 to 350 kg./cm.² with temperature 350 to 550° C., there is a consistent relationship between grade of stainless steel and the intensity of nitriding corrosion, though in the case of a pure NH₃ gas with 100 kg./cm.², 400° C., this relationship is less consistent.

The stainless steel of this invention is not inferior to such high nickel alloys as Hastelloy, Inconel, etc., in its resistance to nitriding under exposure to high-temperature, high-pressure NH₃ gas of high concentration. Moreover, it is cheap and so easy to work that it can be utilized for fabrication of seamless tubes or high pressure vessels. Its weldability is also good; its tensile strength is over 45 kg./mm.² at 450° C., with no susceptibility to hydrogen embrittlement, which is as good as or better than 18 Cr-8 Ni stainless steels.

As clear from the above explanation, the main feature of the present invention is the improvement on the method of protecting industrial apparatus from the corrosive influence of high-temperature, high-pressure NH₃ gas by fabricating said apparatus from a stainless steel of austenitic structure comprising 5 to 12% chromium, 17 to 40% nickel, and the rest mainly iron. Another discovery through this invention is that partial replacement of iron with copper or niobium will further improve the anti-nitriding property of said stainless steel, the preferred addition of copper or niobium being at least 0.5% while an addition of over 4% is undesirable because it greatly impairs the workability of said stainless steel.

Thus another feature of this invention is the protection of the metallic materials of industrial apparatus from the influence of high-temperature, high-pressure NH₃ gas by making that apparatus from a stainless steel of austenitic structure with 5 to 12% chrome, 17 to 40% nickel, 0.5 to 4% copper or niobium, and the rest mainly iron. Three examples of the first embodiment of the invention will now be described:

Example 1

Various test pieces were enclosed in a small autoclave, in which a pure NH₃ gas was circulated under pressure 100 kg./cm.² and temperature 400° C. and after 1000 hours of exposure to said gas they were taken out, measured for a weight gain due to nitriding and observed for the surface condition, with the results as listed in the following table.

Test pieces were 3 x 30 x 50 mm. with austenitic structure.

<table>
<thead>
<tr>
<th>Test piece</th>
<th>Composition</th>
<th>Weight gain due to nitriding (mg/cm.²)</th>
<th>Surface condition after 1000 hr.</th>
<th>Welding after exposure test</th>
</tr>
</thead>
<tbody>
<tr>
<td>No. 1…… 10 Cr-20 Ni……</td>
<td>1.28 1.32</td>
<td>Slight scale under microscope.</td>
<td>Do.</td>
<td>Possible.</td>
</tr>
<tr>
<td>No. 2…… 8 Cr-30 Ni……</td>
<td>1.28 1.78</td>
<td>Macroscopic luster.</td>
<td>Do.</td>
<td>Possible.</td>
</tr>
<tr>
<td>No. 3…… 3 Cr-20 Ni……</td>
<td>1.08 1.61</td>
<td>Metalic luster.</td>
<td>Do.</td>
<td>Possible.</td>
</tr>
<tr>
<td>Control…… 25 Cr-20 Ni……</td>
<td>2.25</td>
<td></td>
<td>Do.</td>
<td>Possible.</td>
</tr>
<tr>
<td>Do…… 20 Cr-35 Ni-Tioloy……</td>
<td>5.02</td>
<td>Exhibits a fragile layer which falls off easily.</td>
<td>Do.</td>
<td>Possible.</td>
</tr>
<tr>
<td>Do…… 10 Cr-40 Ni-Tioloy……</td>
<td>1.10 1.66</td>
<td>Metalic luster.</td>
<td>Do.</td>
<td>Possible.</td>
</tr>
<tr>
<td>Do…… 20 Mo-Ni-Bel-Hastelloy B……</td>
<td>0.80 1.00</td>
<td></td>
<td>Do.</td>
<td>Possible.</td>
</tr>
</tbody>
</table>

In the third column of the above table, the dashes mean that the fragile layer already formed on the surface fell off, resulting in a weight loss.

The degree of nitriding corrosion may be roughly estimated in terms of weight gain. In the case of a large weight gain, the surface nitriding layer will turn into a fragile scale and may fall off. In the case of a small weight gain, the nitriding process will progress relatively quickly and the nitriding rate becomes steadily more sluggish without causing transformation of the surface nitride layer into a scale.

From the above table it is obvious that the resistance to nitriding of what might be called the reverse 18-8 type stainless steel, that is, the opposite of 8 Cr-18 Ni, one which has less Cr and more nickel is extremely more sluggish without causing transformation of the surface nitride layer into a scale.

In an NH₃ synthesizer with a plurality of catalyst layers operating at a pressure of 300 kg./cm.², test pieces were placed and held for about half a year nearly midway between catalyst layers having a gas with about 13% NH₃ concentration, the balance being nitrogen and hydrogen with a molar ratio 1:3, the gas temperature being 500° C. The results of testing for resistance to nitriding were as indicated in the following table.

In this example, the nitriding corrosion of 8 Cr-30 Ni stainless steel was a mere fraction of that of the traditional AISI 304 or AISI 316. The 8 Cr-30 Ni steel exhibited a surface with metallic luster and was weldable after exposure to the harmful gas.

Therefore, if the proposed stainless steel in this invention is adopted for the metallic members of the parts coming into contact with an NH₃ gas of over 10% concentration in the NH₃ synthesizer, the synthesizer can be used for an extremely long period without any repair; and in case of necessity its repair is possible.

Example 3

The proposed 8 Cr-30 Ni stainless steel was employed as the material for a heating tube in which liquid ammonia was circulated at high pressure and the tube was heated from outside and the steel came into contact at the exit of tube with an NH₃ gas with pressure 130 kg./cm.² and temperature 450° C.

Liquid ammonia was delivered by the pump at a rate of 3 kg./hr. under a pressure of 130 kg./cm.² into a stainless heating tube, 20 mm. out. dia., 10 mm. in. dia., 10 m. long, with an effective heating length of about 8 m. The heating electric wire was of about 5KW capacity and the voltage imposed on the wire was so regulated that the NH₃ gas would have a temperature of 450° C. at the exit of tube.

After some 1000 hours of operation, the exit portion of the tube was cut off for inspection of the interior surface and the sectional surface. There was nothing wrong observed except a thin, film nitriding film of metallic luster on the inside surface.

Three examples of the second embodiment of invention, i.e., the composition comprising copper or niobium as a third ingredient will now be described:

Example 4

Various test pieces were enclosed in a small autoclave, in which a pure NH₃ gas was circulated under 100 kg./cm.² at 400° C. After a certain period of exposure to the gas, they were taken out, measured for weight gain due to nitriding, and observed for surface condition, with the following results.
Test pieces were 3 x 30 x 50 mm. and of austenitic structure.

<table>
<thead>
<tr>
<th>Test pieces</th>
<th>Composition</th>
<th>Weight gain due to nitriding (mg/cm²)</th>
<th>Surface condition after 1,000 hr.</th>
</tr>
</thead>
<tbody>
<tr>
<td>No. 1</td>
<td>10 Cr-20 Ni-2 Cu</td>
<td>1.14</td>
<td>Do</td>
</tr>
<tr>
<td>No. 2</td>
<td>5Cr-15 Ni-3 Cu</td>
<td>0.89</td>
<td>Do</td>
</tr>
<tr>
<td>No. 3</td>
<td>5 Cr-3 Ni-4.2 Nh</td>
<td>1.00</td>
<td>Do</td>
</tr>
<tr>
<td>Control</td>
<td>5 Cr-20 Ni</td>
<td>1.88</td>
<td>Do</td>
</tr>
</tbody>
</table>

The above table clearly shows that the stainless steel comprising 5 to 12% chromium and 17 to 40% nickel is itself an excellent anti-nitriding steel, but a small addition of copper with further improve its anti-nitriding property. 0.5 to 4% addition of copper will reduce the weight gain of steel due to nitriding to about 3% of that in steel with no copper content, and will further strengthen the nitriding film with the metallic luster of surface being maintained for a long period.

The mechanism of such improvement on the anti-nitriding property of stainless steel through a small addition of copper is not well elucidated; probably, copper may be negatively catalytic to nitriding. Though not so much as copper, niobium, too, is effective for improvement of anti-nitriding property.

The sectional structures of the test pieces in this example never exhibited any evidence of hydrogen embrittlement and exhibited a resistance to hydrogen embrittlement which is the same as that of the proposed stainless steel which constitutes the first embodiment of this invention and contains no copper or niobium.

**Example 5**

In an NH₃ synthesizer with a plurality of catalyzer layers operating at a pressure of 300 kg/cm², test pieces were placed and held for about half a year nearly midway between catalyzer layers having a gas with about 13% NH₃ concentration, the balance being nitrogen and hydrogen with a molar ratio 1:3, the gas temperature being 500°C.

The results of testing for resistance to nitriding were as indicated in the following table.

<table>
<thead>
<tr>
<th>Test pieces</th>
<th>Composition or name</th>
<th>Corrosion due to nitriding (thickness of nitriding layer), mm./yr.</th>
<th>Welding after exposure test</th>
</tr>
</thead>
<tbody>
<tr>
<td>No. 4</td>
<td>8 Cr-30 Ni-4 Cu</td>
<td>0.01</td>
<td>Possible, 0.02</td>
</tr>
<tr>
<td>Control</td>
<td>AISI 304</td>
<td>0.1</td>
<td>Impossible</td>
</tr>
</tbody>
</table>

The nitriding corrosion of the 8 Cr-30 Ni-4 Cu stainless steel proposed as a second embodiment of this invention was a mere tenth of that in the conventional AISI 304 or half of that in the 8 Cr-30 Ni steel constituting the first embodiment of this invention. Even after exposure to NH₃ atmosphere, the 8 Cr-30 Ni-4 Cu steel retained a surface of metallic luster and was found weldable.

Therefore, if the proposed stainless steel in this example is adopted for the metallic member of those members coming into contact with an NH₃ gas of over 10% concentration in an NH₃ synthesizer, the synthesizer can be used for an extremely long period without any repair; and in case of necessity its repair is possible.

**Example 6**

The proposed 8 Cr-30 Ni-3 Cu stainless steel was employed as the material for a heating tube in which, under the same conditions and using the same device as in Example 3, liquid ammonia, was circulated at 3 kg/hr under pressure of 130 kg/cm² and heated from the outside by an electric wire of 5 kw. capacity in such manner that the NH₃ gas temperature at the exit of the tube would be 450°C.

After about 1500 hours of operation, the exit portion of heating tube was cut off to inspect the interior surface and the sectional surface. There was nothing wrong observed except a thin nitriding film of metallic luster on the inside surface.

What is claimed is:

1. In the process of exposing metallic articles to high pressure ammonia gas, the step of contacting said metallic articles with ammonia gas of over 10% concentration, at a pressure of 50-350 kg/cm² at a temperature of 350-550°C, while having at least their exposed portions which contact said gas, formed from an alloy having improved corrosion and nitriding resistance, consisting essentially of 5-12% chromium, 17-40% nickel, and the balance substantially all iron.

2. In the process of claim 1 the improvement wherein said metallic articles are containers.

3. In the process of claim 1 the improvement wherein said metallic articles are pressure vessels.

4. In the process of claim 1 the improvement wherein said metallic articles are formed from an alloy consisting essentially of 5-12% chromium, 17-40% nickel, 0.5-4% of a metal selected from the group consisting of copper and niobium, and the balance substantially all iron.

5. In the process of claim 4 the improvement wherein said metallic articles are containers.

6. In the process of claim 4 the improvement wherein said metallic articles are pressure vessels.

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<th>Description</th>
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DAVID L. RECK, Primary Examiner.
P. WEINSTEIN, Assistant Examiner.
UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,362,855

Mitsuo Shimo et al.

January 9, 1968

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

In the heading to the printed specification, lines 8 and 9, for "assignors to Nissan Kagaku, Kogyo Kabushiki Kaisha, Tokyo, Japan" read -- assignors, by direct and mesne assignments, of one-half to Nissan Kagaku Kogyo Kabushiki Kaisha and one-half to Nippon Yakin Kogyo Kabushiki Kaisha, both of Tokyo, Japan --.

Signed and sealed this 29th day of April 1969.

(SEAL)

Attest:

Edward M. Fletcher, Jr.
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents