1. Introduction

Nitrogen addition to stainless steels has great influence on mechanical properties as well as corrosion resistance. However, the nitriding rate by N2 gas is significantly small and also the attainable nitrogen contents in Fe–Cr alloys is less than 1 mass% in general. In the present study, aiming for the enhancement of the nitriding rate and the increase of nitrogen contents more than 1 mass%, NH3 and N2 solution nitriding of Fe–Cr alloys under various conditions has been carried out and their behaviors of nitrogen absorption in Fe–Cr alloys are investigated. It is found that the suppression of the pre-decomposition of NH3 before it reaches the sample is critical for the effective NH3 nitriding.

In the solid solution state, nitrogen increases with increasing Cr or Mn content in steel. Thus, high nitrogen stainless steels can be easily produced by applying the solid solution nitriding method to high Cr or Mn stainless steels. However, this process has a big drawback. Namely, the nitriding rate by N2 gas is significantly small even at around 1 473 K. By assuming that N diffusion process is the rate controlling step, the calculated phase development in the Fe–23.8mass%Cr sheet by N2 nitriding (0.1 MPa) at 1 473 K is shown in Fig. 1. In the calculation, the surface concentration of nitrogen is assumed to be that of the equilibrium concentration. It takes about 10 h for the production of the ultra-high nitrogen steel. The term ultra high nitrogen steel is generally related to nitrogen contents higher than 1 mass% in ferritic matrix.

On the other hand, the studies about nitriding process in the solid solution state have been widely carried out as an alternative high nitrogen steel fabrication process. This is a simple and powerful method to obtain high nitrogen steel without the problem of blow holes and special equipments for pressurized melting. Actually, Nakamura and Takaki reported that a ferritic stainless steel with a composition of Fe–Cr absorbs nitrogen up to 1.0 mass% and transforms to austenitic stainless steel (Fe–23Cr–1N) by simple annealing process in nitrogen atmosphere of 0.1 MPa at 1 473 K.

It is well known that the soluble nitrogen content increases with increasing Cr or Mn content in steel. Thus, high nitrogen stainless steels can be easily produced by applying the solid solution nitriding method to high Cr or Mn stainless steels. However, this process has a big drawback. Namely, the nitriding rate by N2 gas is significantly small even at around 1 473 K. By assuming that N diffusion process is the rate controlling step, the calculated γ phase development in the Fe–23.8mass%Cr sheet by N2 nitriding (0.1 MPa) at 1 473 K is shown in Fig. 1. In the calculation, the surface concentration of nitrogen is assumed to be that of the equilibrium concentration. It takes about 10 h for the production of the ultra-high nitrogen steel. The term ultra high nitrogen steel is generally related to nitrogen contents higher than 1 mass% in ferritic matrix.

KEY WORDS: high nitrogen stainless steel; nickel-free austenitic stainless steel; nitrogen-alloying; NH3 solid solution nitriding.
development of $\gamma$ phase of 400 $\mu$m thickness. Consequently, $N_2$ solid solution nitriding method can only be applied for very thin wire or sheet production, but not for the mass production.

If we use $\text{NH}_3$-$\text{H}_2$ gas mixture instead of $\text{N}_2$ gas for nitriding stainless steel, however, quite higher nitriding rate can be expected, since $\text{NH}_3$ has significantly higher nitrogen potential than that of $\text{N}_2$ due to the instability of $\text{NH}_3$ relative to $\text{N}_2$ and $\text{H}_2$. Despite of its attractive feature, few studies about $\text{NH}_3$ solid solution nitriding at high temperature more than 1 273 K have been carried out. At high temperature more than 1 273 K, $\text{NH}_3$ gas easily decomposes into $\text{N}_2$ and $\text{H}_2$ gases, especially at the metallic Fe surface, before $\text{NH}_3$ reaches the reacting surface. Once the decomposition takes place, it may have rather lower nitriding potential than pure $\text{N}_2$ has. Therefore, for the successful $\text{NH}_3$ nitriding process of steels, the restraint of $\text{NH}_3$ pre-decomposition before it reaches the steel is the most important factor for achieving higher nitriding rate and $N$ contents.

In the present study, by using devised $\text{NH}_3$ gas injection system to minimize the pre-decomposition, austenitic Fe–23.5Cr alloy with more than 3 mass% of nitrogen that had never been achieved by solution nitriding was successfully produced.

2. Thermodynamic Background

The equilibrium content of the nitrogen in stainless steel under a particular partial pressure of $N_2$ has been well studied by Tsuchiya et al. It depends on three variables of states: temperature $T$, nitrogen partial pressure $P_{N_2}$, and alloy composition of the steel. In the present study, temperature is fixed at 1 473 K and Cr content and corresponding $P_{N_2}$ (or $\text{NH}_3/\text{H}_2$ ratio) are considered as variables. In a nitrogen atmosphere the dissolution of nitrogen in the steel is governed by the reaction

$$\frac{1}{2} \text{N}_2 = [N]$$

where $[N]$ is the dissolved nitrogen content in stainless steel. Yielding the equilibrium constant for a given temperature,

$$K_N = \frac{a_N}{\sqrt{P_{N_2}}} = \frac{f_N [N]}{\sqrt{P_{N_2}}}$$

where $K_N$ is the equilibrium constant of the reaction (1), $a_N$ is the activity of the dissolved nitrogen and $f_N$ is the activity coefficient of nitrogen. By assuming the validity of Sieverts’ law, the solubility of $N$ in $\gamma$-Fe in the range of 1 323 K $\leq T \leq$ 1 523 K can be evaluated based on the following equation,

$$\log K_N = \frac{625}{T} - 2.093 = -1.6687$$

In a dilute solution of nitrogen in pure iron $f_N$ reaches unity. In combination with Eqs. (2) and (3) at 1 473 K,

$$\log \frac{f_N [N]}{\sqrt{P_{N_2}}} = -1.6687$$

From Eq. (1), equilibrium $[N]$ with a particular $P_{N_2}$ can be calculated.

The nitriding potential of $\text{NH}_3$–$\text{H}_2$ gas mixture can be expressed by the corresponding partial pressure of $N_2$ based on the reaction

$$\text{NH}_3 = \frac{1}{2} \text{N}_2 + \frac{3}{2} \text{H}_2$$

$$\Delta G^o = 53 670 - 120.2 T \text{ (J/mol)}$$

At 1 473 K,

$$\sqrt{P_{N_2}} = 15 201 \frac{P_{\text{NH}_3}}{P_{\text{H}_2}^1}$$

The calculated $P_{N_2}$ corresponding to $\text{NH}_3$–$\text{H}_2$ gas mixtures based on Eq. (6) is shown in Table 1. These calculated extraordinary high pressures are not actually measurable, rather better to be interpreted that $\text{NH}_3$ gas has a significantly large nitriding potential corresponding to such high pressure.

The influence of content of dissolved $\text{Cr}$ wt% on the $a_N$ can be evaluated by introducing the interaction parameters. A Taylor series expansion leads to the first and second order interaction parameters $e_N^C$ and $r_N^C$ including the effect of nitrogen on itself. $e_N^C$, $r_N^C$

$$\log f_N^C = e_N^C \text{Cr} + r_N^C \text{Cr}^2 + e_N^K [N]$$

The interaction parameter of $e_N^C$ at 1 473 K has not been established so far. In the present study, instead of the interaction parameter of $e_N^C$, an interaction parameter $e_N^K$ was used as a first approximation. The interaction parameters in austenite at 1 473 K used in this study are shown in Table 2. In combination with Eqs. (4), (6) and (7),

$$\log [N] = \log \sqrt{P_{N_2}} - 1.6687 - e_N^K [N] - e_N^K \text{Cr}^2 - r_N^K \text{Cr}^2$$

It is noted that Eq. (8) can be used to estimate $N$ solubility in the $\gamma$-phase. Once nitrides are formed, however, Eq. (8) cannot be applicable. From Eq. (8), the equilibrium nitrogen contents in a particular Fe–Cr stainless steel at 1 473 K can be calculated as a function of chromium content and the partial pressure of nitrogen. The equilibrium nitrogen contents as a function of Cr content in Fe–Cr alloy with various partial pressure of $N_2$ is shown in Fig. 2. The N content required for chromium nitride formation is also shown in Fig. 2. Namely, the N contents with $N_2$ from 0.25 to 20.0 MPa are just hypothetical values calculated from

Fig. 1. Nitrogen diffusion profile of Fe–23.5Cr stainless steel by nitriding with $N_2$ (0.1 MPa) at 1 473 K.
Table 1. Corresponding N$_2$ gas pressure calculated by Eq.(6).

<table>
<thead>
<tr>
<th>Partial Pressure</th>
<th>Corresponding P$_{N_2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>15% NH$_3$+H$_2$</td>
<td>290.9 MPa</td>
</tr>
<tr>
<td>20% NH$_3$+H$_2$</td>
<td>424.8 MPa</td>
</tr>
<tr>
<td>30% NH$_3$+H$_2$</td>
<td>778.6 MPa</td>
</tr>
</tbody>
</table>

Table 2. Interaction parameters in austenite used in this study at 1473 K.$^{5}$

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$e_N^{C_p}$</td>
<td>-9.0 x 10$^5$</td>
</tr>
<tr>
<td>$e_N^{C}$</td>
<td>7.6 x 10$^5$</td>
</tr>
<tr>
<td>$e_N^{S}$</td>
<td>8.5 x 10$^5$</td>
</tr>
</tbody>
</table>

Fig. 2. Equilibrium nitrogen contents at various partial pressure of N$_2$ as a function of chromium content at 1473 K.

Eq. (8).

3. Experimental

3.1. Materials

Two kinds of steels are used for the solution nitriding. The main difference of these steels is their chromium contents, which is closely related with the soluble nitrogen contents and final microstructure after nitriding. The chemical composition is shown in Table 3.

Material A was commercial SUS430 stainless steel of 0.35 mm thin sheet. Material B was produced by induction melting in vacuum and then casting into a 200 H11003 200 H11003 H11003 200 mm cubic mold. This ingot was cut to 10 mm thick plates by a band saw, then sliced into the sheet of 100 mm H11003 10 H11003 1mm. Finally, the sheets were ground and polished to 0.9 mm thickness to remove the thermally damaged part caused during cutting.

3.2. Apparatus and Procedure

Nitriding experiments were performed in a vertical alumina tube furnace. The schematic view of experimental system is shown in Fig. 3. It mainly consisted of gas delivery system and a reacting furnace. Unreacted NH$_3$ gas was cracked into N$_2$ and H$_2$ by passing tangled Fe mesh wire at 773 K. The reacting gas was directly injected onto the surface through a side hole (3 mm diameter) in the one-end of Al$_2$O$_3$ tube. The specimen was suspended by a specimen holder. The distance between the side hole and the specimen surface was adjusted to be about 5 mm. This gas injection system makes it possible to minimize the pre-decomposition of ammonia. The schematic view of the specimen holder and the gas injection tube is shown in Fig. 4. The specimen holder was introduced for water quenching without breaking airtight condition.

Each flow rate of gases was controlled by using mass flow rate controllers. In the present study, the total flow rate was always fixed to be 300 mL/min. Table 4 shows gas mixtures used in the present study. Ar, H$_2$ and N$_2$ gases were purified by drierite (CaSO$_4$) and Mg de-oxidation furnace (at 723 K). NH$_3$ was originally purified to 99.9999% and no further purified process was applied.

Before nitriding, Ar gas purging in the system was carried out for more than 4 h. After that, under Ar–5%H$_2$ atmosphere, the specimen was heated to 150°C and held for 5 min. Then, it was heated to 1200°C and held for 30 min. After that, nitriding gas was introduced to the furnace for pre-arranged nitriding time. After nitriding for a particular
time, the specimen was quenched by dropping into a water bath. The Ms point of Material B is less than room temperature so that Martensite phase was not formed. In the case of material A, some amount of Martensite phase was formed due to its high Ms point (485 K).9)

The specified area of the specimen (about 10 mm/H11003 10 mm) had distinctively shining surface where the reacting gas was supposed to be effectively injected. Thus, this part of the sample was cut into 10×10 mm and subjected to the analyses.

3.3. Analysis

Nitrogen and hydrogen contents were analyzed by inert gas fusion method and solid-state thermal conductivity technology, respectively. About 0.05 g of sample which had been sliced in advance was used to examine the nitrogen content. 0.534 mass% N standard sample (LECO) was used for calibration. In a particular nitriding condition, samples contained chromium nitrides after nitriding. The nitrogen contents measured by using the inert gas fusion method were the overall nitrogen content including that of the nitride.

The microstructure was observed with an optical microscope and FE-SEM. Grain size and austenitic transformation was examined by the electron backscatter diffraction (EBSD). Nitride phases were analyzed by energy dispersive spectroscopy (EDS).

4. Results and Discussion

4.1. N2 and NH3 Solid Solution Nitriding

Absorbed N contents in material A (Fe–15Cr and 0.35 mm thickness) after 30 min under various nitriding gas mixtures at 1473 K are shown in Fig. 5. The N contents increased with an increase in nitriding potential. Namely, NH3 nitriding is quite effective to establish high N contents than N2 (1 atm) nitriding just as expected before. The overall N content of 3 mass% was easily achieved by 30 min nitriding treatment, when NH3 (90%)–H2 gas mixture was used for nitriding. The N content shown in Fig. 5 with NH3 more than 50% contains the nitrogen of Cr2N, since Cr2N is possibly formed with more than 0.9 mass% of N content.

The measured average N contents in material B (Fe–23.8Cr and 0.9 mm thickness) after NH3 nitriding for 20 h at 1473 K with various nitrogen potentials and that by N2 (1 atm) nitriding for 20 h are shown in Fig. 6. The N content required for Cr2N formation is also shown in Fig. 6.

Refer to the corresponding PN2 shown in Table 1, however, the observed N contents by NH3 nitriding shown in Figs. 5 and 6 are far below than that expected from the extraordinary high nitrogen potential of NH3–H2 gas mixtures. There are several possible reasons; (1) pre-decomposition of NH3, (2) slow NH3 decomposition rate on the chromium nitride covered surface, (3) slow reaction rate of chromium nitride formation, and (4) slow N diffusion rate in the chromium nitride layer. Since the aim of the present study is to find out the feasibility of NH3 nitriding, the kinetic study of NH3 nitriding is left for the future study.

The change in the average nitrogen content with time in material B during N2 gas (0.1 MPa) nitriding at 1473 K is shown in Fig. 7 by a solid line. The N content increases with increase of nitriding time and levels off after 10 h and finally reached near equilibrium value of about 1.1 mass% of N after 20 h.

The dotted line in Fig. 7 shows the change in the average nitrogen content in material B as a function of time by NH3 (30%) nitriding at 1473 K. Differently from the N2 (0.1 MPa) nitriding, the evaluation of equilibrium N content by NH3 nitriding is practically impossible because of Cr2N formation.

Unfortunately, due to the technical problem of the furnace, no measurements of N contents between 1 and 20 h were carried out. Comparing the N contents after 1 h nitrid-
ing in Fig. 7, however, it can be certainly said that the NH$_3$ (30%) nitriding rate is about 5 times faster than that of N$_2$ (0.1 MPa) nitriding. From these results, it can be said that NH$_3$ nitriding makes it possible to obtain high N contents and high nitriding rate compared with N$_2$ nitriding.

Figure 8 shows the measured nitrogen contents in the isothermal section of Fe–Cr–N ternary system obtained under various nitrogen potentials for 20 h at 1473 K. The isothermal section of Fe–Cr–N ternary system at 1473 K is calculated by FactSage. Point a was obtained by 1 h 50% NH$_3$ nitriding of material A sample. Points b, c, d and e corresponded to the N contents obtained by 20 h nitriding of material B sample with 30%, 20%, 15% NH$_3$, and N$_2$ respectively.

As shown in Fig. 8, samples at the points of a, b and c must contain chrome nitride of CrN or Cr$_2$N. The optical micrograph of the sample at the point b is shown in Fig. 9. It shows the lamellar structure and is confirmed to include nitrides (mainly Cr$_2$N) by EDS analysis. The same nitride structure (mainly CrN) is also found in the material A treated with 50% NH$_3$ nitriding for 1 h (point a in Fig. 8).

4.2. CrN and Cr$_2$N Formation

Nitride precipitation in austenite matrix is generally detrimental because the nitrides are consuming chromium and consequently corrosion resistance will be decreased. Nitride precipitation have little influence on the yield and ultimate strength, but pronounced effect to reduce material plasticity which results in embrittlement during uniaxial and impact loading. The nitride formation can be avoided by using low $P_{NH_3}$ nitriding. Under this condition, high nitriding rate and high nitrogen contents will not be achieved.

The isothermal section of Fe–Cr–N ternary system at 1573 K is shown in Fig. 9. The γ-phase area is extensively increased at 1573 K. The solubility of N in γ-phase with Fe–24Cr alloy is found to be about 3.2 mass%. The Fe–23.8Cr–1.9N alloy (point C in Fig. 8) was annealed in Ar atmosphere at 1573 K for 3 h. Most of nitride formed at 1473 K was found to be dissolved into austenitic matrix by annealing.

Thus, Fe–Cr–N alloys with more than 3 mass% of nitrogen without CrN can be produced by NH$_3$ nitriding at 1573 K.

4.3. Possibility of Hydrogen Absorption

During the nitriding with NH$_3$, hydrogen dissolution reaction may occur, according to the following reaction

$$NH_3(g) \rightarrow 3H(g) \text{ in } \gamma-Fe + N_2(g)/2$$

It is well known that hydrogen is a detrimental element in steels due to hydrogen embrittlement. In the bright annealing process of stainless steel by N$_2$–H$_2$ gas mixtures at around 1273 K, however, the solubility of hydrogen in stainless steels is found to be negligibly small. In the pres-
ent study, the solubility of H in the Fe–Cr alloy was experimentally examined by 1 h NH₃ and N₂ nitriding at 1 473 K. Figure 11 shows hydrogen contents of as received material A (Fe15.4Cr), material A with nitriding by N₂–5%H₂ gas mixture and material A with nitriding by NH₃–50%H₂ gas mixture. As shown in Fig. 11, only 1.5 ppm hydrogen increase was detected even using 50% H₂ contained nitriding gas mixture. Thus, it can be said that hydrogen dissolution in stainless steels during NH₃ nitriding processing is negligible even at 1 473 K.

5. Conclusions

To establish solid solution nitriding in a practical process, NH₃ solution nitriding of Fe–Cr alloys at 1 473 K has been investigated. The results are summarized as follows:

(1) Using devised NH₃ gas injection system to minimize the pre-decomposition of NH₃ gas, austenitic Fe–23.5Cr alloys with more than 3 mass% of nitrogen (ultra high nitrogen stainless steel) that had never been achieved by solution nitriding was successfully produced.

(2) Chromium nitrides (CrN or Cr₂N) are formed in γ matrix by NH₃ nitriding with more than 20% of P_{NH₃} after 20 h at 1 473 K. The nitride formation behavior is well explained from the phase stability diagram of Fe–Cr–N system.

(3) The high nitrogen stainless steel of more than 3 mass% N without nitrides will be produced directly by NH₃ nitriding at 1 573 K.

(4) Hydrogen dissolution during NH₃ nitriding at 1 473 K is found to be negligible.

(5) NH₃ nitriding can be a promising method to produce ultra high nitrogen stainless steels.

REFERENCES