Fabrication of Ultrahigh Nitrogen Austenitic Steels by Nitrogen Gas Absorption into Solid Solution

T. TSUCHIYAMA, H. ITO, K. KATAOKA, and S. TAKAKI

For the purpose of fabricating ultrahigh nitrogen austenitic steels ($>$1 mass pct N), the phenomenon of nitrogen absorption into solid solution was thermodynamically analyzed and applied to Fe-Cr-Mn system ternary alloy. During the annealing of the steel in a nitrogen gas atmosphere of 0.1 MPa at 1473 K (nitrogen absorption treatment), the nitrogen content of the steel was increased with the absorption of nitrogen gas from the material surface and then saturated when the system reached a state of equilibrium. Effect of the steel composition on an equilibrium nitrogen content was formulated taking account of interactions among Cr, Mn, and N atoms, and the condition for fabrication of ultrahigh nitrogen austenitic steels was clarified. The nitrogen addition to ultrahigh content markedly increased proof stress and tensile stress of the austenitic steels without losing moderate ductility. For example, Fe-24Cr-10Mn-1.43N (mass pct) alloy has 830 MPa in 0.2 pct proof stress, 2.2 GPa in true tensile stress, and 75 pct in total elongation. As a result of tensile tests for various nitrogen-bearing austenitic steels, it was found that the proof stress is increased in proportion to (atomic fraction of nitrogen)$^{2/3}$.

I. INTRODUCTION

NITROGEN addition to austenitic stainless steels has many advantages including that (1) the strength of the steels is greatly increased without lowering ductility too much;[1,2] (2) nickel content can be reduced because nitrogen is a strong austenite stabilizer, which markedly lowers the M_s temperature;[3,4] and (3) corrosion resistance, especially pitting corrosion resistance, is also improved.[1,4,5] Therefore, the processing and properties of high nitrogen stainless steels have being widely studied for the purpose of complying with the increased demands on stainless steels for structures in chemical and energy industries,[6,7] marine and offshore environments,[7,8] surgical and dental applications,9 and so on. However, the nitrogen content of the industrially produced materials is 0.4 pct at most, that is to say, we do not make the most of the advantages of nitrogen addition. Development of the technique to add more nitrogen could improve the properties of austenitic stainless steels further.

In general, high nitrogen stainless steels are usually produced by melting in a high-pressurized nitrogen gas atmosphere. There is a report that a stainless steel containing solute nitrogen of 1.1 pct had been made using 4 MPa nitrogen gas.[10] However, the pressurized melting process requires special equipment, and, besides, it sometimes causes the problem of formation of blowholes on solidification.[11] This prevents the increase of nitrogen to the ultrahigh concentration region. (In this article, steels containing over 1 pct N are referred to as "ultrahigh nitrogen steels.") On the other hand, the addition of nitrogen by gas absorption into steel at solid state (nitrogen absorption treatment) easily enables the production of high nitrogen steels without the problem of blowholes, because the solubility of nitrogen is much larger in austenite than in original ferrite.[12] Actually, Nakamura and Takaki[13] reported that a ferritic stainless steel with a composition of Fe-23Cr absorbs nitrogen up to 1.0 pct and forms stable austenitic structure through a simple annealing in a 0.1 MPa (1 atm) nitrogen gas atmosphere at 1473 K. Although the effect of chemical composition on the behavior of nitrogen absorption into solid steel has been hardly investigated quantitatively in Fe-Cr-Mn ternary system alloys, it is well known that the soluble nitrogen content is increased with increasing Cr or Mn content in molten steel.[14,15] Thus, it is expected that more addition of Cr or Mn to base steels should markedly increase the absorbed nitrogen content at solid state as well.

In this study, for the purpose of production of the Fe-Cr-Mn-N system ultrahigh nitrogen austenitic stainless steels by the nitrogen absorption treatment, the absorbed equilibrium nitrogen content is formulated as a function of Cr and Mn content on the basis of thermodynamics taking account of interactions among Cr, Mn, and N atoms. From the information obtained, the condition for the absorption of ultrahigh content nitrogen was clarified. The mechanical properties of the developed steels were also investigated by means of tensile testing, and then the effect of the N-N interaction on the proof stress was discussed in the ultrahigh nitrogen austenitic steels.

*Throughout this article, the chemical composition is expressed in mass percent, unless otherwise stated.

II. EXPERIMENTAL PROCEDURE

Fe-(12 to 24) pct Cr- (0 to 30) pct Mn alloys for the nitrogen absorption treatment were prepared by ark melting in an argon gas atmosphere. The specimens were hot rolled by a reduction

T. TSUCHIYAMA, Lecturer, and S. TAKAKI, Professor, are with the Department of Materials Science and Engineering, Kyushu University, Fukuoka 812–8581, Japan. Contact e-mail: *toshi@zaiko.kyushu-u.ac.jp* H. ITO, formerly Graduate Student, Department of Materials Science and Engineering, Kyushu University, is Researcher with Toyo Kohan Co. Ltd., Kudamatsu 744-8611, Japan. K. KATAOKA, formerly Graduate Student, Department of Materials Science and Engineering, Kyushu University, is Researcher with Hitachi Metals, Ltd., Yasugi 692-8601, Japan.

Manuscript submitted November 20, 2002.

of about 50 pct at 1473 K, homogenized at 1573 K for 7.2 ks,* and then hot rolled again at 1073 to 1323 K to 0.25

---

*For some specimens in which δ ferrite is formed at 1573 K, the homogenization was performed at 1473 K for 18 ks.

---

to 3.0 mm in thickness. These plate specimens obtained were electrically polished with a solution of phosphoric acid and chromic oxide ($H_3PO_4:CrO_3 = 2:1$), and then annealed at 1473 K in a nitrogen gas atmosphere of 0.1 MPa for 1.8 to 216 ks (nitrogen absorption treatment). The temperature of 1473 K was selected by considering the sufficient amount of diffusivity, the wide solubility of nitrogen, and the practical viewpoint. Chemical compositions (mainly N, Cr, and Mn) of the steels were analyzed after the nitrogen absorption treatment. Microstructure was examined by means of X-ray diffractometry and optical microscopy. Tensile tests were carried out with an Instron-type testing machine at a strain rate of 3.3×10^{-3}/s for the plate specimens (gage: 3-mm width $\times$ 6-mm $\times$ length 1-mm thickness). Grain size of the specimens for the tensile tests was controlled to be around 100 μm through the recrystallization; cold rolling from 3- to 1-mm thick and the annealing at 1473 K for a short time (0 to 0.6 ks) followed by water cooling. The numerical analysis on nitrogen absorption behavior was carried out using the mathematical software, *Mathematica 4.*

III.   RESULTS AND DISCUSSION

A. *Thermodynamics on Nitrogen Gas Absorption into Solid Solution*

Upon annealing of steel in a nitrogen gas atmosphere, nitrogen atoms are absorbed into the solid solution from the material surface and cause some microstructural changes such as phase transformation or precipitation of nitrides. For example, Figure 1 shows a change in the average nitrogen content of a 0.35-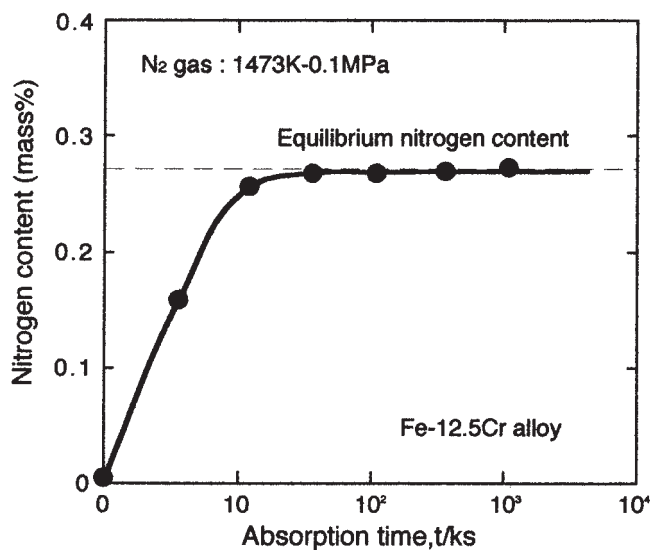mm thick ferritic stainless steel sheet (Fe-12.5Cr low-carbon alloy) during annealing in a N_2 gas atmosphere of 1473 K–0.1 MPa (nitrogen absorption treatment). The nitrogen content increases with the absorption treatment time and then levels off at 0.27 pct after the absorption treatment for 3.6 ks. This saturated nitrogen content is settled by the activity balance of nitrogen between the N_2 gas and the solid solution; in other words, the nitrogen is absorbed until the system reaches a state of equilibrium. Figure 2 represents a Fe-Cr-N ternary isothermal phase diagram at 1473 K. The 12.5 Cr steel transforms with the nitrogen absorption from ferrite single phase $\rightarrow$ (ferrite + austenite) two phase $\rightarrow$ austenite single phase. However, nitrogen is not concentrated to the higher nitrogen region of the (austenite + nitride) under the condition of 0.1 MPa N_2 gas, because the system reaches equilibrium state in the austenite single-phase region. The dashed line in the figure shows the equilibrium nitrogen content confirmed in 12 to 23 Cr steels.[16]

Thermodynamics on the nitrogen absorption phenomenon is explained as follows.[17] When a pure iron and an Fe-M1-M2-... multisystem alloy are annealed in a N_2 gas atmosphere of 0.1 MPa (Figure 3), nitrogen atoms are absorbed into each steel and the nitrogen content is increased to the equilibrium content. In this case, N_2 gas pressure is constant, thus, the activity of nitrogen must be the same between the two materials under the equilibrium state. The activity of nitrogen, a_N, is described as a function of nitrogen concentration, [pct N], as follows:

$$a_N = f_N[\text{pct N}] \qquad [1]$$

where f_N is the Henrian activity coefficient. Letting the activity coefficients in the pure iron and the Fe-M1-M2-... multisystem alloy be $f_N^{(Fe)}$ and $f_N^{(alloy)}$ respectively, the following relation is held between equilibrium nitrogen concentrations [pct $N^{(Fe)}$] and [pct $N^{(alloy)}$].

$$f_N^{(Fe)} [\text{pct } N^{(Fe)}] = f_N^{(alloy)} [\text{pct } N^{(alloy)}] \qquad [2]$$

Fig. 1—Change in average nitrogen content of 12.5Cr ferritic stainless steel sheet (0.35 mm thick) during annealing in a N_2 gas atmosphere of 1473 K–0.1 MPa.
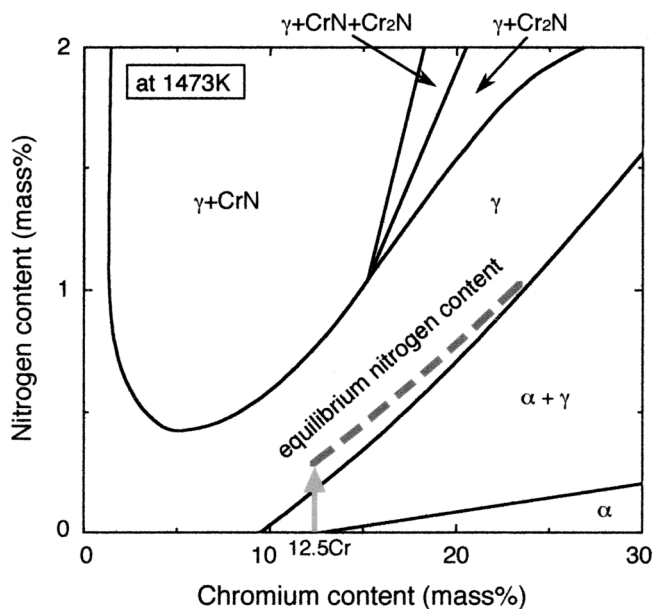

Fig. 2—Isothermal phase diagram at 1473 K in Fe-Cr-N ternary alloy. The dashed line shows equilibrium nitrogen content.
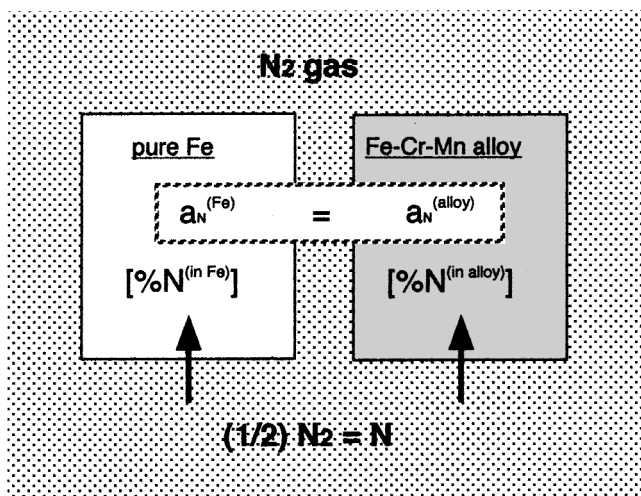
Fig. 3—Schematic illustration showing the nitrogen absorption phenomenon. The a_N denotes activity of nitrogen in the materials.

Since the soluble nitrogen concentration is very low in pure iron, we can accept the equation of

$$f_N^{(Fe)} = 1 \quad [3]$$

Besides, the equilibrium nitrogen concentration in pure iron was reported by Imai:[17]

$$[pct\ N^{(Fe)}] = 0.0223\ pct\ (at\ 1473\ K) \quad [4]$$

Therefore, the [pct $N^{(alloy)}$] can be obtained if the activity coefficient of the alloy $f_N^{(alloy)}$ is found. Describing the interaction coefficient of alloy component X as $f_N^{(X)}$, the $f_N^{(alloy)}$ is given by

$$f_N^{(alloy)} = f_N^{[N]} f_N^{[M1]} f_N^{[M2]} \ldots \quad [5]$$

Expansion of Eq. [5] (in regular logarithm form) to the secondary terms on each alloying component gives

$$\log f_N^{(alloy)} = \log f_N^{[N]} + \log f_N^{[M1]} + \log f_N^{[M2]} + \ldots$$
$$= e_N^{[N]}\ [pct\ N] + r_N^{[N]}\ [pct\ N]^2$$
$$+ e_N^{[M1]}\ [pct\ M1] + r_N^{[M1]}\ [pct\ M1]^2$$
$$+ e_N^{[M2]}\ [pct\ M2] + r_N^{[M2]}\ [pct\ M2]^2 + \ldots$$
$$+ w_N^{[N,M1]}\ [pct\ N]\ [pct\ M1] + w_N^{[N,M2]}\ [pct\ N]$$
$$[pct\ M2] + w_N^{[M1,M2]}[pct\ M1]\ [pct\ M2] + \ldots \quad [6]$$

where $e_N^{[X]}$, $r_N^{[X]}$, $w_N^{[X,Y]}$ are the interaction parameters of alloy component X and Y on nitrogen. Substitution of Eq. [3], [4], and [6] into Eq. [2] in regular logarithm form gives

$$\log[pct\ N^{(alloy)}] = \log f_N^{(Fe)} + \log[pct\ N^{(Fe)}] - \log f_N^{(alloy)}$$
$$= -1.65 - e_N^{[N]}\ [pct\ N] - r_N^{[N]}\ [pct\ N]^2$$
$$- e_N^{[M1]}\ [pct\ M1] - r_N^{[M1]}\ [pct\ M1]^2$$
$$- e_N^{[M2]}\ [pct\ M2] - r_N^{[M2]}\ [pct\ M2]^2 - \ldots$$
$$- W_N^{[N,M1]}\ [pct\ N]\ [pct\ M1] - w_N^{[N,M2]}$$
$$[pct\ N]\ [pct\ M2] - w_N^{[M1,M2]}$$
$$[pct\ M1]\ [pct\ M2] - \ldots \quad [7]$$

In the case of low nitrogen steels, the terms of [pct N] can be removed and the [pct $N^{(alloy)}$] is almost estimated by the following equation:

$$\log[pct\ N^{(alloy)}]$$
$$= -1.65 - e_N^{[M1]}\ [pct\ M1] - r_N^{[M1]}\ [pct\ M1]^2$$
$$- e_N^{[M2]}\ [pct\ M2] - r_N^{[M2]}\ [pct\ M2]^2 - \ldots$$
$$- W_N^{[M1,M2]}\ [pct\ M1]\ [pct\ M2] - \ldots \quad [8]$$

B. Behavior of Nitrogen Absorption into Fe-Cr-Mn Ternary System Alloys

Chemical compositions of base steels applied to the nitrogen absorption treatment and the equilibrium nitrogen contents absorbed into the steels are listed in Table I (under 1473 K–0.1 MPa). The equilibrium nitrogen content tends to be increased with increasing Cr or Mn content. In order to clarify the individual effect of the alloying elements on the nitrogen absorption behavior, the equilibrium nitrogen contents are plotted for Fe-Cr and Fe-Mn binary base alloys as a function of Cr or Mn content in Figure 4. Although both elements enlarge the equilibrium nitrogen content, it is found that the Cr addition is much more effective than the Mn addition for increasing nitrogen content. For example, Cr addition of 23 pct or more increases the nitrogen content to ultrahigh nitrogen level (>1 pct), while the Mn addition as much as over 25 pct only does to 0.2 pct at most. However, it is well known that Mn addition is effective for making high nitrogen steels;[15] thus, the combination of Cr and Mn addition seems to enlarge the equilibrium nitrogen content. Figure 5 shows the equilibrium nitrogen contents in Fe-20 pct Mn ($\pm$1 pct)-Cr ternary base alloy as a function of Cr content with the bold curve. This figure also represents the results for Fe-Cr and Fe-Mn binary base alloys by the gray curves (shown in Figure 4) and that shifted upward from the Fe-Cr curve by the equilibrium nitrogen content in the Fe-20 pct Mn alloy (about 0.1 pct N) with the broken line. It should be noted that the nitrogen content experimentally measured in the Fe-20 pct Mn-Cr alloy (bold curve) is much more than that expected by the simple addition (broken line). This means the combination of Cr and Mn addition markedly promotes the nitrogen absorption in the steels, which reflects the effect of the nonlinear term of $W_N^{[M1,M2]}$ [pct M1][pct M2] in Eq. [7]. This term means that there is some interaction among three kinds of atoms: Cr, Mn, and N.

The effect of Cr and Mn on the equilibrium nitrogen content can be formulated in terms of the thermodynamics, as mentioned previously. Putting M1 and M2 in Eq. [7] as Cr and Mn, respectively, the equilibrium nitrogen content is expressed for Fe-Cr-Mn-N system austenitic steels as follows:

$$\log[pct\ N]$$
$$= -1.65 - e_N^{[N]}\ [pct\ N] - r_N^{[N]}\ [pct\ N]^2$$
$$- e_N^{[N]}\ [pct\ N] - r_N^{[N]}\ [pct\ N]^2 - e_N^{[Cr]}\ [pct\ Cr]$$
$$- r_N^{[Cr]}\ [pct\ Cr]^2 - e_N^{[Mn]}\ [pct\ Mn] - r_N^{[Mn]}$$
$$[pct\ Mn]^2 - W_N^{[N,Cr]}\ [pct\ N]\ [pct\ Cr] - W_N^{[N,Mn]}$$
$$[pct\ N][pct\ Mn] - W_N^{[Cr,Mn]}\ [pct\ Cr]\ [pct\ Mn] \quad [9]$$

Table I. Chemical Compositions of Base Steels Applied to the Nitrogen Absorption Treatment and the Equilibrium Nitrogen Contents (under 1473 K–0.1 MPa) Absorbed into the Steels

| Base Steel Composition (Mass Percent)		Equilibrium N Content (Mass Percent)
Cr	Mn	
11.64	—	0.249
12.24	—	0.300
15.39	—	0.425
17.52	—	0.520
18.08	—	0.576
18.63	—	0.645
19.74	—	0.734
20.11	—	0.613
21.61	—	0.833
22.78	—	0.875
23.48	—	0.985
24.18	—	1.016
—	1.0	0.026
—	2.0	0.028
—	3.0	0.030
—	4.7	0.035
—	7.0	0.040
—	10.0	0.050
—	12.0	0.060
—	15.0	0.073
—	17.0	0.080
—	20.0	0.110
—	24.0	0.140
—	32.0	0.214
11.66	20.68	0.726
11.67	14.59	0.543
11.70	19.50	0.690
11.83	5.46	0.355
11.83	14.57	0.550
11.92	18.25	0.659
12.00	9.89	0.437
12.15	30.19	1.115
15.61	10.15	0.702
15.73	5.31	0.565
15.86	19.61	1.044
15.89	18.37	1.002
16.06	19.30	1.018
16.17	14.05	0.859
16.25	9.82	0.696
18.28	15.54	1.106
18.29	15.33	1.090
19.56	4.95	0.842
19.73	19.04	1.433
19.76	11.08	1.042
19.86	14.21	1.176
19.88	10.90	1.050
22.03	12.61	1.299
22.19	5.55	1.080
23.03	18.40	1.774
23.05	5.25	1.166
23.32	9.53	1.326
23.99	10.01	1.470
24.03	20.49	1.949
24.05	9.92	1.438
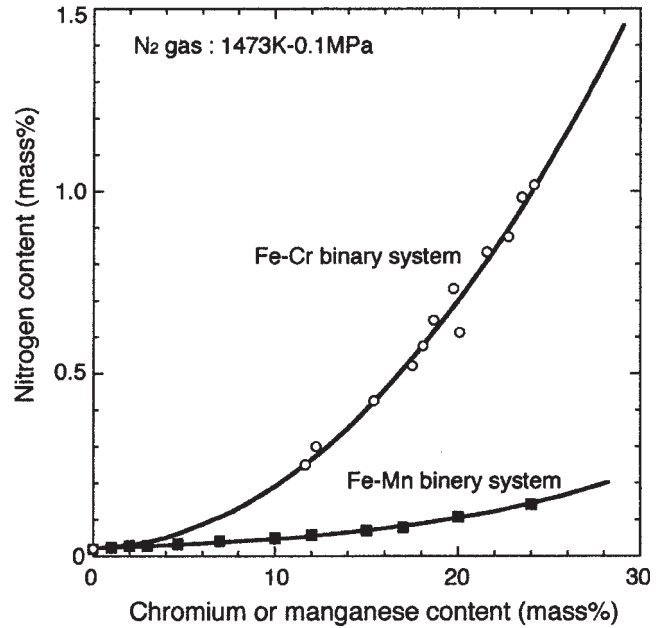
Fig. 4—Relations between equilibrium nitrogen content at 1473 K and Cr or Mn content in the Fe-Cr and Fe-Mn binary alloys.
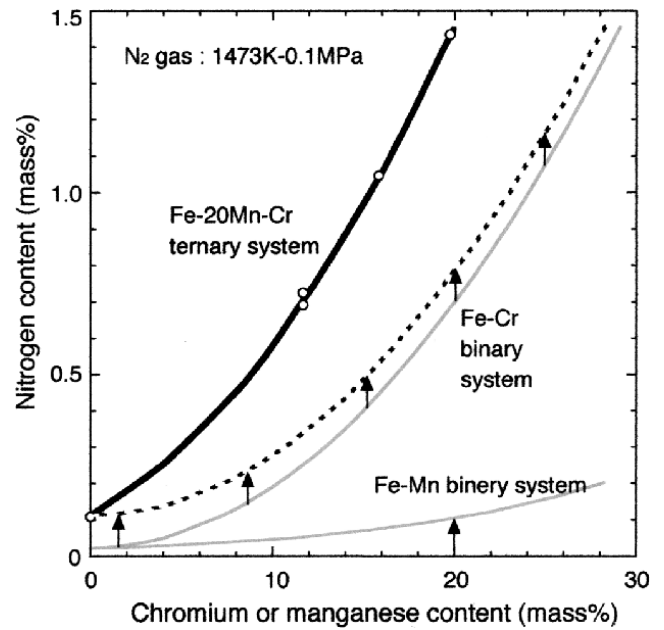

Fig. 5—Relations between equilibrium nitrogen content at 1473 K and Cr content in Fe-10Mn-Cr ternary alloys. The results in Fig. 4 are also represented by the gray curves.

Also, this is rewritten as follows in the case of low-Cr low-Mn alloys in which the nitrogen content is not high:

$$\log[\text{pct N}]$$
$$= -1.65 - e_N^{[\text{Cr}]}[\text{pct Cr}] - r_N^{[\text{Cr}]}[\text{pct Cr}]^2$$
$$- e_N^{[\text{Mn}]}[\text{pct Mn}] - r_N^{[\text{Mn}]}[\text{pct Mn}]^2$$
$$- W_N^{[\text{Cr,Mn}]}[\text{pct Cr}][\text{pct Mn}] \qquad [10]$$

Table II. Activity Parameters of Nitrogen in Austenite at 1473 K Used in This Study[13,14]

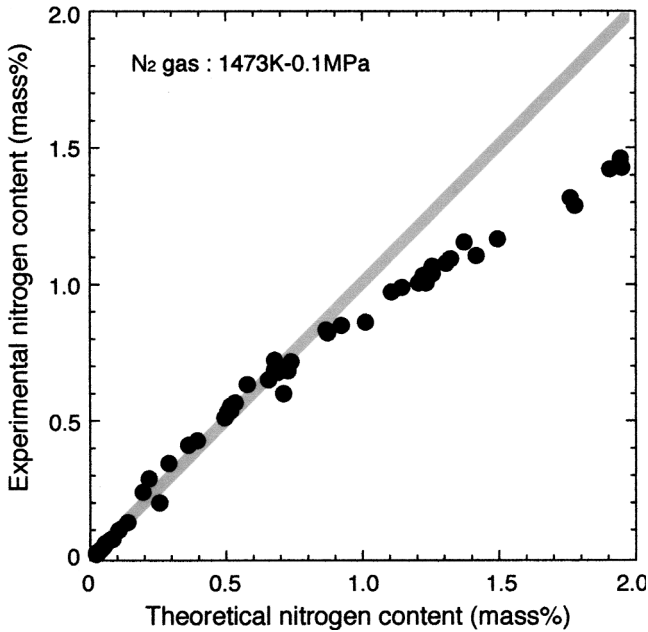|	
$e_N^{[Cr]}$	-9.0×10^{-2}
$r_N^{[Cr]}$	7.6×10^{-4}
$e_N^{[Mn]}$	-3.4×10^{-2}
$r_N^{[Mn]}$	2.59×10^{-5}
$w_N^{[Cr.Mn]}$	5.0×10^{-4}

Fig. 6—Relation between experimentally measured equilibrium nitrogen content and theoretical one without considering N-N interaction: [pct N] = $10^{(-1.65 + 9.0 \times 10^{-2}[pct\ Cr] - 7.6 \times 10^{-4}[pct\ Cr]^2 + 3.4 \times 10^{-2}[pct\ Mn] - 2.59 \times 10^{-5}[pct\ Mn]^2 - 5.0 \times 10^{-4}[pct\ Cr][pct\ Mn])}$ mass pct.

Although there are various reported values for the activity parameters of nitrogen in austenite, those shown in Table II[17,18] were used in this study considering the fitting in the low nitrogen region between experimental data and theoretical values. Figure 6 shows the relation between the experimental equilibrium content and the theoretical one given by Eq. [10]; $10^{(-1.65 - e_N^{[Cr]}[pct\ Cr] - r_N^{[Cr]}[pct\ Cr]^2 - e_N^{[Mn]}[pct\ Mn] - r_N^{[Mn]}[pct\ Mn]^2 - W_N^{[Cr,Mn]}[pct\ Cr][pct\ Mn])}$. There is a satisfactory correspondence in the result up to about 0.8 pct N. However, it is found that, in the high nitrogen region, nitrogen is not absorbed to the expected value estimated by Eq. [10]. This deviation seems to be mainly due to N-N interaction in the high nitrogen region; thus, the most effective term regarding nitrogen content in Eq. [9], $e_N^{[N]}$[pct N], is taken into account and Eq. [10] is modified as follows:

$$\log[pct\ N]$$
$$= -1.65 - e_N^{[N]}[pct\ N]$$
$$- e_N^{[Cr]}[pct\ Cr] - r_N^{[Cr]}[pct\ Cr]^2 - e_N^{[Mn]}[pct\ Mn]$$
$$- r_N^{[Mn]}[pct\ Mn]^2 - W_N^{[Cr,Mn]}[pct\ Cr][pct\ Mn] \quad [11]$$

The solution in Eq. [12] for [pct N] with the interaction parameters in Table II gives the equilibrium nitrogen content as a function of Cr and Mn contents.
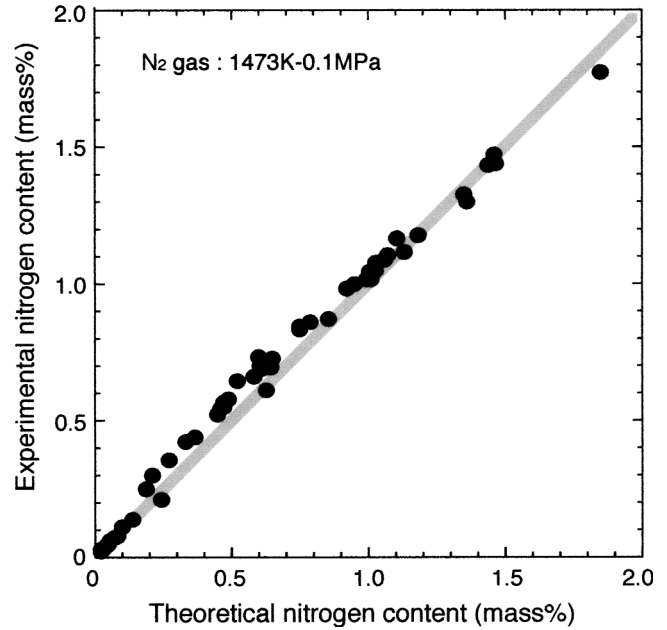

Fig. 7—Relation between the experimentally measured equilibrium nitrogen content and the theoretical one considering N-N interaction: [pct N] = 5.11 product log $\{0.196 \times 10^{(-1.65 + 9.0 \times 10^{-2}[pct\ Cr] - 7.6 \times 10^{-4}[pct\ Cr]^2 + 3.4 \times 10^{-2}[pct\ Mn] - 2.59 \times 10^{-5}[pct\ Mn]^2 - 5.0 \times 10^{-4}[pct\ Cr][pct\ Mn])}\}$ mass pct.

$$[pct\ N]$$
$$= 5.11\ product\ log\ \{0.196 \times 10^\wedge(-1.65 + 9.0$$
$$\times 10^{-2}[pct\ Cr] - 7.6 \times 10^{-4}[pct\ Cr] + 3.4$$
$$\times 10^{-2}[pct\ Mn] - 2.59 \times 10^{-5}[pct\ Mn]^2 - 5.0$$
$$\times 10^{-4}[pct\ Cr][pct\ Mn])\} \quad (at\ 1473\ K) \quad [12]$$

Here, instead of the interaction parameter of $e_N^{[N]}$, an interaction parameter on N-C, $e_N^{[C]} = 0.085$,[17] was substituted because we have no data on $e_N^{[N]}$ (at 1473 K) so far. Figure 7 shows the relation between theoretical and experimental equilibrium nitrogen contents obtained by Eq. [12]. The theoretical values successfully agree with the experimental ones under any nitrogen content: therefore, we can predict the content of nitrogen absorbed into Fe-Cr-Mn alloys by annealing at 1473 K with this equation. Figure 8 displays the iso-equilibrium nitrogen content diagram (1473 K–0.1 MPa) drawn with Eq. [12]. In the hatched area, ultrahigh nitrogen steels can be obtained. The condition is approximately given by

$$2.1\ [pct\ Cr] + [pct\ Mn] > 50 \quad [13]$$

---

*The product log function gives the solution for x in $f = xe^x$.[19] The solution for [pct N] in Eq. [11], log pct N = a [pct N] + b (a and b = constants), is expressed as [pct N] = $-\{product\ log\ (-10^b\ a\ \ln 10)\}/(a\ \ln 10)$, and this corresponds to Eq. [12].

C. Microstructural change with nitrogen absorption into solid solution

In the Fe-Cr-Mn system alloys, the microstructure before the nitrogen absorption treatment depends on Cr and Mn contents, and some alloys have austenitic structure but most
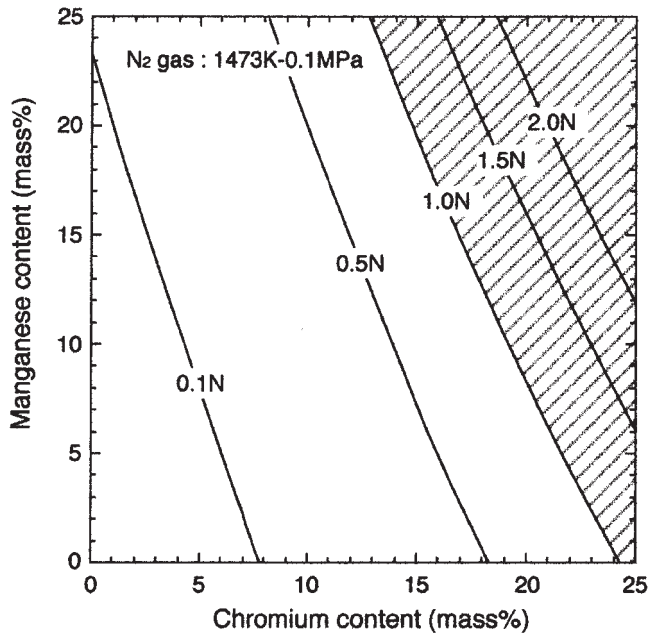
Fig. 8—Iso-equilibrium nitrogen content diagram (1473 K–0.1 MPa) in Fe-Cr-Mn system ternary alloy.

Fig. 9—Structure diagram (room temperature) of Fe-Cr-Mn system ternary alloy before the nitrogen absorption treatment.

other alloys have ferritic or martensitic structure. Figure 9 shows the structure diagram of Fe-Cr-Mn system alloy before the nitrogen absorption treatment. In the high-Cr low-Mn region, the microstructure is ferritic because the alloys are not austenitized even at the solution treatment temperature. On the other hand, the low-Cr high-Mn alloys are fully austenitized at the temperature; thus, the microstructure obtained after cooling is of austenite single structure or mixed structure composed of retained austenite and martensite of bcc α' or hcp ε depending on their M_s temperature.

For these specimens, the nitrogen absorption treatment was performed under the condition of 1473 K–0.1 MPa N_2 gas and then water cooled from the temperature. Figures 10 and 11 show the structure diagram and examples of optical micrographs of the nitrogen-absorbed specimens, respectively. All alloys shown in Figure 10 were confirmed to be austenitized at 1473 K after the absorption of nitrogen. After water cooling from the nitrogen absorption treatment temperature, austenite single structure is obtained in the hatched area (Figure 11(a)), while martensite single structure or mixed structure of austenite and martensite was also obtained in the low-Cr regions (Figures 11(b) and (c)). Looking at Figure 10 together with Figure 8, any ultrahigh nitrogen steel (1< pct N) is realized to have stable austenitic single structure. Figure 12 shows the relation between lattice parameter and nitrogen content in the produced steels with austenitic single structure. Some data of Fe-18Cr-10Ni alloys with various nitrogen contents were also used in the low nitrogen region. The lattice parameter, a (in nanometers), linearly increases with increasing nitrogen content, [pct N] (in at. pct), irrespective of alloy system up to the ultrahigh nitrogen region. That is, a quasi-Vegard's law is held for these alloys. The linear relation is expressed as
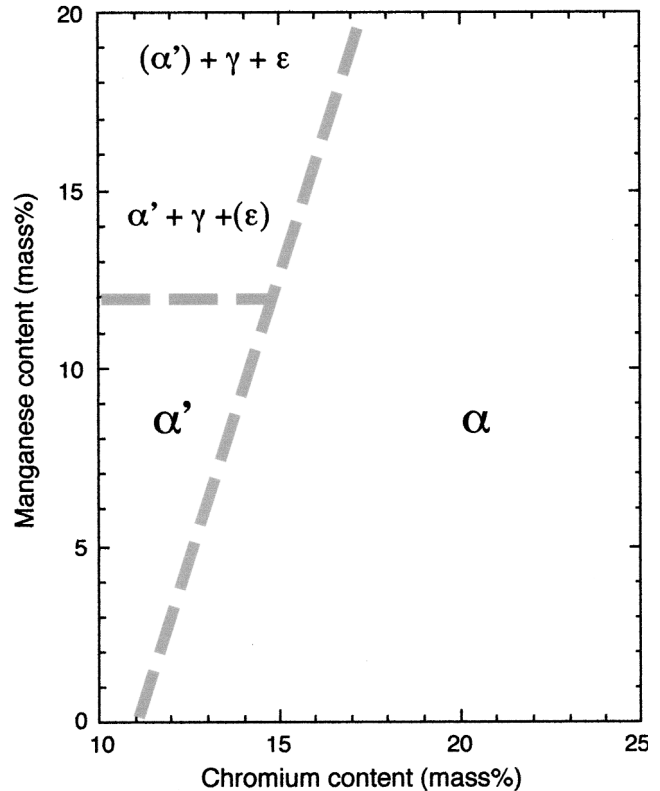
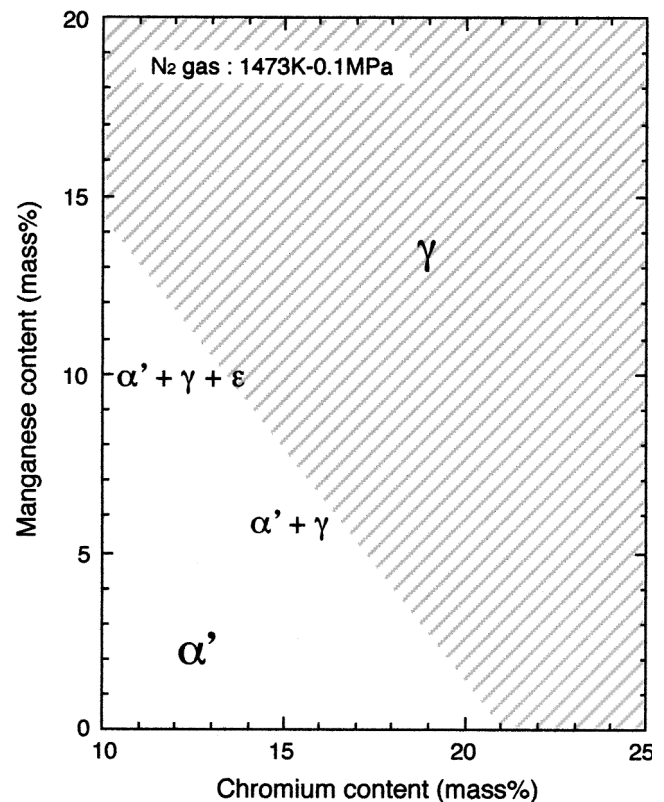$$a = 0.3587 + 0.0010 \text{ [at. pct N]} \qquad [14]$$

Fig. 10—Structure diagram (room temperature) of the nitrogen-absorbed Fe-Cr-Mn alloy. The nitrogen absorption treatment was carried out at 1473 K–0.1 MPa, followed by water cooling.
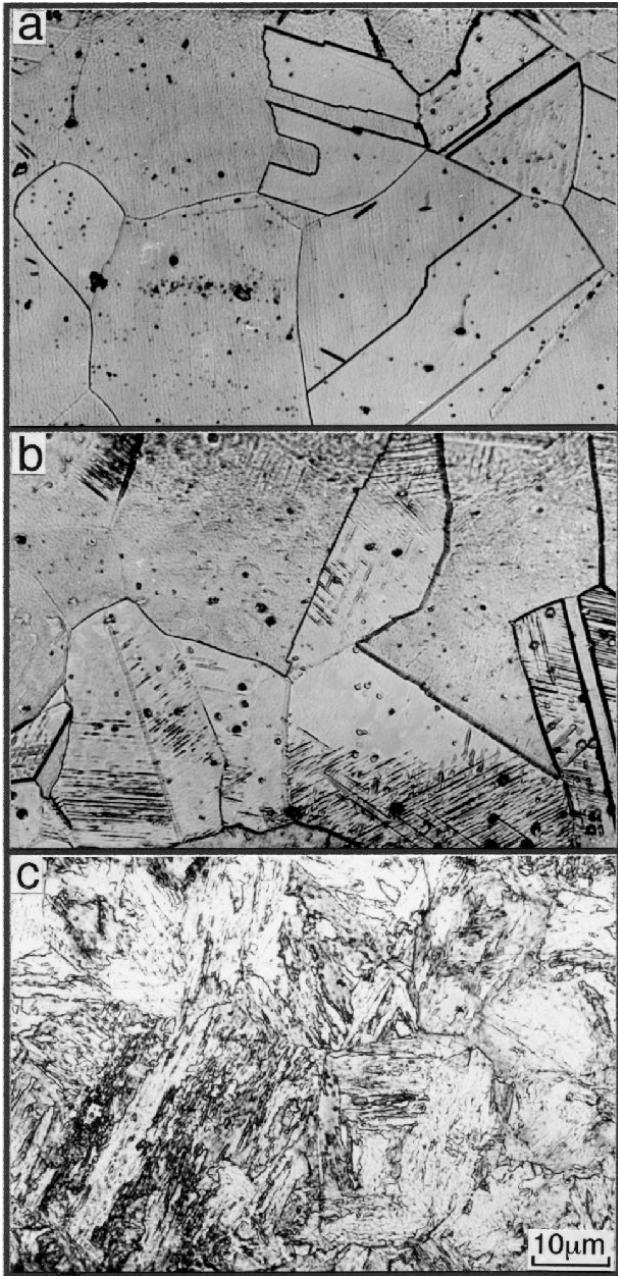
Fig. 11—Optical micrographs of the nitrogen-absorbed Fe-Cr-Mn alloys: (*a*) Fe-24Cr-10Mn-1.43N, (*b*) Fe-12Cr-10Mn-0.43N, and (*c*) Fe-12Cr-0.25N. The nitrogen absorption treatment was carried out at 1473 K–0.1 MPa, followed by water cooling.

From the fact that the law is satisfied even for the steel with the highest nitrogen content obtained in this study (Fe-24Cr-20Mn-1.95 N), it can be stated that no precipitate of nitride exists and all of the nitrogen is in solution in all of the alloys.

D. *Tensile Property of Ultrahigh Nitrogen Austenitic Stainless Steels*

Figure 13 represents true stress–true strain curves of two kinds of ultrahigh nitrogen austenitic stainless steels (Fe-20Cr-11Mn-1.05 N and Fe-24Cr-10Mn-1.43N). A result of conventional N-free austenitic stainless steel
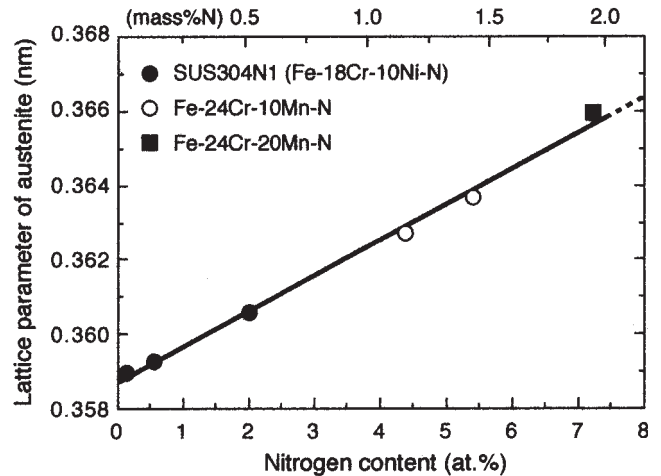

Fig. 12—Relation between lattice parameter and nitrogen content in the various nitrogen-bearing steels with austenitic single structure.
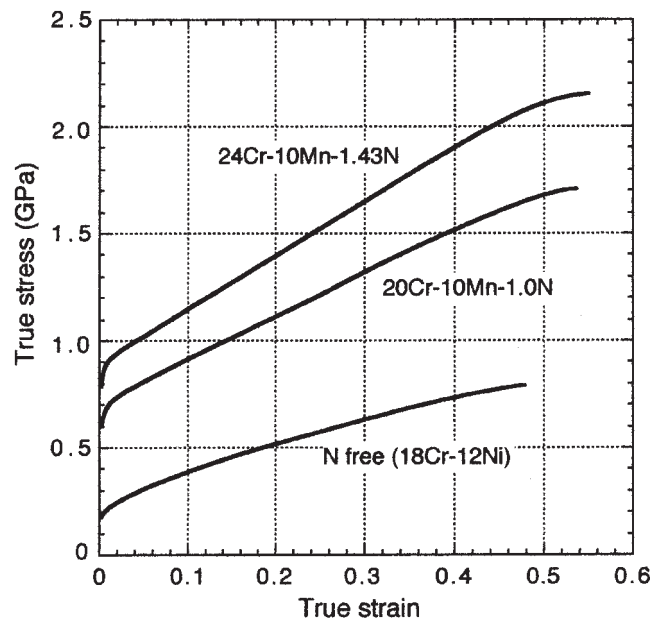

Fig. 13—True stress–true strain curves of Fe-20Cr-11Mn-1.05N, Fe-24Cr-10Mn-1.43N, and N-free Fe-18Cr-12Ni alloys.

(Fe-18Cr-12Ni) is also shown for reference. The strength is markedly raised owing to the solid solution strengthening by nitrogen. For example, the proof stress and the tensile stress for the 1.43 pct N steel are 830 MPa and 2.2 GPa in true stress, respectively. In spite of such a high strength, the total elongation of 75 pct is obtained. Since nitrogen enlarges not only the strength but also the, work-hardening rate of austenite,[20] the occurrence of local necking is thought to be suppressed and the uniform deformation became possible to the high strain region in the ultrahigh nitrogen steels. Figure 14 shows the 0.2 pct proof stress of the Cr-Mn-N system high-nitrogen steels and the Cr-Ni-N system low-nitrogen steels,[21] which are produced by the nitrogen absorption treatment, as a function of the square root of solute nitrogen content in atomic fraction. The proof stress is increased with increasing
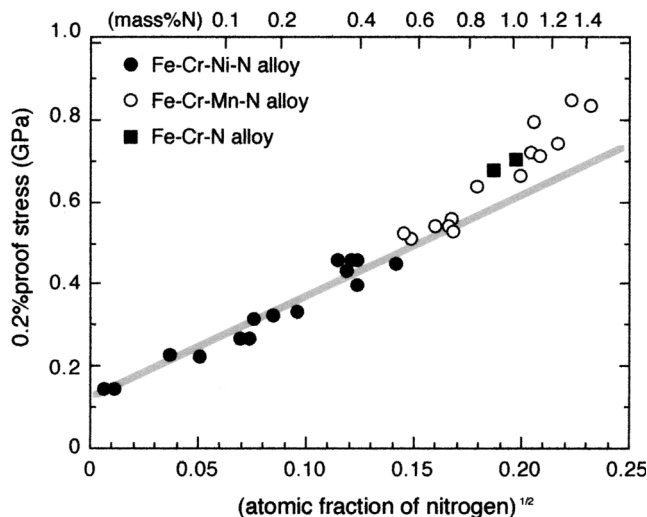
Fig. 14—Relation between 0.2 pct proof stress and nitrogen content, (atomic fraction)$^{1/2}$, in the Cr-Mn-N system high-nitrogen steels and the Cr-Ni-N system low-nitrogen steels, which are produced by the nitrogen absorption treatment.

Fig. 15—Relation between 0.2 pct proof stress and nitrogen content, (atomic fraction)$^{2/3}$, in the Cr-Mn-N system high-nitrogen steels and the Cr-Ni-N system low-nitrogen steels, which are produced by the nitrogen absorption treatment.

nitrogen content along the single curve. Although the high nitrogen steels contain a large amount of substitutional alloying elements, Cr or Mn, the solid solution strengthening by them can be regarded as small and the effect of nitrogen seems to be predominant in the strength. In general, it is known that the proof stress of steels strengthened by solid solution strengthening has a linear relationship to the square root of the alloying element content in the case of low concentration. The theory on the strengthening mechanism was proposed by Fleischer.[22] He obtained the relationship that the critical share stress is proportional to the square root of the concentration of solute atoms assuming that only one solute atom participate in a unit process of a dislocation movement. In fact, there are many reports on the experimental results exhibiting the linear relationship between the proof stress and the square root of solute nitrogen content in various nitrogen steels[23,24,25] as well as the present results in the low nitrogen region (<0.6 pct N). However, in the high nitrogen region over 0.6 pct N, the data clearly deviate from the linear relationship upward higher strength. This means that plural nitrogen atoms participate in the unit process of a dislocation movement in the high nitrogen steels because the elastic lattice stress fields by nitrogen atoms can overlap each other. In such case, the critical shear stress is often proportional to the concentration of solute atoms (atomic fraction) to the power 2 over 3, as explained by Lubusch's theory.[26] Figure 15 shows the proof stress in Figure 14 as a function of (atomic fraction of N)$^{2/3}$. In all specimens used in this study containing up to 1.4 pct, the linear relationship is obtained. As a result, the 0.2 pct proof stress of high nitrogen austenitic steel is expressed as follows:

$$\sigma_{0.2} \text{ [GPa]} = 0.14 + 4.8 \text{ [N]}^{2/3} \quad \text{([N]:atomic fraction)} \quad [15]$$

With this formula, the proof stress can be predicted even in the ultrahigh nitrogen region.

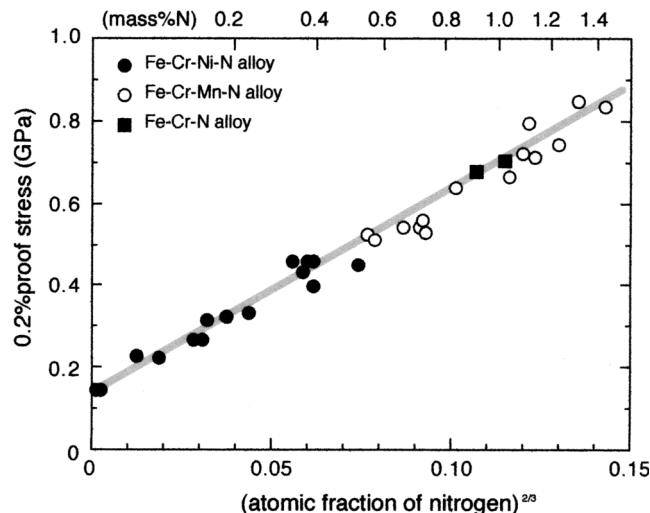As mentioned previously, the nitrogen absorption into solid solution easily enables us to produce ultrahigh nitrogen austenitic stainless steels containing over 1 pct N and to increase the proof stress of austenite to more than 0.8 GPa. However, it takes a rather long time for the treatment; thus, this method could be industrially applied only to thin plate or wire material. To develop larger-sized materials in the future, the research on the combination of the powder metallurgy technique with the nitrogen absorption treatment[13,27,28] must be more important.

IV. CONCLUSIONS

1. Nitrogen is absorbed into steel at solid state from the material surface during annealing in a nitrogen gas atmosphere at high temperature. The nitrogen content of the steel is increased with the annealing time but saturated when the system reaches the state of equilibrium, which depends on the chemical composition of the steel.
2. The annealing in a nitrogen gas atmosphere at 0.1 MPa (nitrogen absorption treatment) easily enables us to produce ultrahigh nitrogen steels (>1 mass pct N) without using high-pressurized nitrogen gas.
3. The saturated nitrogen content is thermodynamically expressed as a function of chemical composition of the steel. In the case of nitrogen absorption under 1473 K–0.1 MPa in Fe-Cr-Mn ternary alloys, the saturated nitrogen content is estimated with the equation as

[pct N]

$$= 5.11 \text{ product log } \{0.196 \times 10^{(-1.65 + 9.0 \times 10^{-2}[\text{pct Cr}]} $$
$$-7.6 \times 10^{-4}[\text{pct Cr}]^2 + 3.4 \times 10^{-2}[\text{pct Mn}] - 2.59 \times 10^{-5}[\text{pct Mn}]^2 - 5.0$$
$$\times 10^{-4}[\text{pct Cr}][\text{pct Mn}])\}$$

According to this equation, it is found that the ultrahigh nitrogen steels can be obtained under the condition of

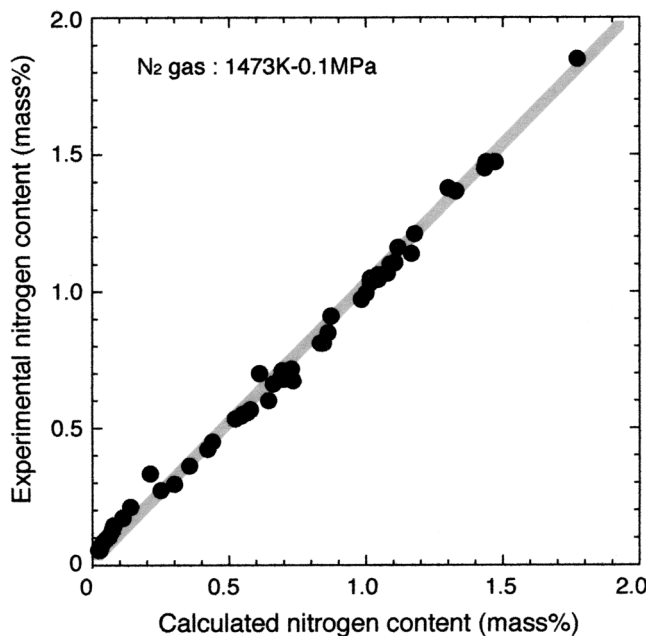$$2.1[\text{pct Cr}] + [\text{pct Mn}] > 50$$

Fig. 16—Relation between the experimentally measured equilibrium nitrogen content and the calculated one with Eq. [A1]: [pct N] = 0.9 exp{1.7 × (−1.65 + 9.0 × 10⁻²[pct Cr] −7.6 × 10⁻⁴[pct Cr]² + 3.4 × 10⁻²[pct Mn] −2.59 × 10⁻⁵[pct Mn]² −5.0 × 10⁻⁴[pct Cr][pct Mn])}.

4. The ultrahigh nitrogen steels have stable austenitic structure. The mechanical properties of the steels are characterized by the much higher strength than conventional austenitic stainless steels and the moderate ductility achieved by high work hardening rate by solute nitrogen. The 0.2 pct proof stress of the nitrogen bearing austenitic steels is expressed as

$$\sigma_{0.2} \text{ [GPa]} = 0.14 + 4.8[\text{N}]^{2/3} \qquad ([\text{N}]\text{:atomic fraction})$$

APPENDIX

Since the product log function has a similar form as the exponential function, Eq. [12] can be rewritten to the next usable equation by doing proper fitting operation.

$$
\begin{aligned}
[\text{N}] &= 0.9 \exp\{1.7 \times (-1.65 + 9.0 \times 10^{-2} \text{ [pct Cr]} - 7.6 \\
&\quad \times 10^{-4} \text{ [pct Cr]}^2 + 3.4 \times 10^{-2} \text{ [pct Mn]} - 2.59 \\
&\quad \times 10^{-5} \text{ [pct Mn]}^2 - 5.0 \\
&\quad \times 10^{-4} \text{ [pct Cr] [pct Mn]}\} \quad \text{(at 1473 K)} \qquad [\text{A1}]
\end{aligned}
$$

Figure 16 shows the relation between the experimentally measured equilibrium nitrogen content and the calculated one with Eq. [A1]. Although this is a semiempirical equation, the equilibrium nitrogen concentration in Fe-Cr-Mn system alloys can be easily estimated without using the uncommon function.

REFERENCES

1. M.O. Spiedel: *Proc. Int. Conf. on Stainless Steels,* ISIJ, Chiba, 1991, pp. 25-35.
2. V.G. Gavriljuk and H. Berns: *High Nitrogen Steels—Structure, Properties, Manufacture, Applications,* Springer, Berlin, 1999, pp. 169-73.
3. G.E. Eichelman, Jr. and F.C. Hull: *Trans. ASM,* 1953, vol. 45, pp. 77-104.
4. R.P. Reed: *JOM,* 1989, Mar., pp. 16-21.
5. K. Osozawa: *J. Jpn. Soc. Heat Treatment,* 1996, vol. 36, pp. 206-12.
6. G. Stein, I. Hucklenbroich, and M. Wagner: *Materials Science Forum,* Trans Tech Publications, Uetikon-Zuerich, 1999, vols. 318-320, pp. 167-73.
7. J. Sundvall, J. Olsson, and B. Holmberg: *Materials Science Forum,* Trans Tech Publications, Uetikon-Zuerich, 1999, vols. 318-320, pp. 181-86.
8. J.D. Fritz and R.J. Gerlock: *Desalination,* 2001, vol. 135, pp. 93-97.
9. G. Stein, I. Hucklenbroich, and H. Feichtinger: *Materials Science Forum,* Trans Tech Publications, Uetikon-Zuerich, 1999, vols. 318-320, pp. 151-60.
10. Y. Katada, S. Sagara, Y. Kobayashi, and T. Kodama: *Proc. 1st Int. Conf. on Advanced Structural Steels (ICASS2002),* NIMS, Tsukuba, 2002, pp. 317-18.
11. V.G. Gavriljuk and H. Berns: *High Nitrogen Steels—Structure, Properties, Manufacture, Applications,* Springer, Berlin, 1999, pp. 206-13.
12. H.K. Feichtinger: *Proc. Int. Conf. on Stainless Steels,* ISIJ, Chiba, 1991, pp. 1125-32.
13. N. Nakamura and S. Takaki: *Iron Steel Inst. Jpn. Int.,* 1996, vol. 36, pp. 922-26.
14. A.H. Satir-Kolorz and H.K. Feichtinger: *Z. Metallkde.,* 1991, vol. 82, pp. 689-97.
15. J.C. Rawers and L.J. Rawers: *J. Mater. Sci. Lett.,* 1991, vol. 10, pp. 1101-02.
16. S. Takaki and N. Nakamura: *Materials Science Forum,* Trans Tech Publications, Uetikon-Zuerich, 1999, vols. 318-320, pp. 723-31.
17. Y. Imai: *Nitrogen-Alloyed Steels—Fundamentals and Applications,* AGNE, Tokyo, 1994, pp. 31-34.
18. J. Kunze: *Nitrogen and Carbon in Iron and Steel—Thermodynamics,* Akademie Verlag, Berlin, 1990, p. 133.
19. S. Wolfram: *The Mathematica Book,* 4th, ed. Cambridge University Press, Cambridge, 1999, chap. 3.2.10.
20. S. Kubota, Y. Xia, and Y. Tomota: *Iron Steel Inst. Jpn.* Int., 1998, vol. 38, pp. 474-81.
21. S. Takaki, T. Tsuchiyama, H. Ito, and K. Kataoka: *CAMP-ISIJ,* 2000, vol. 13, p. 364.
22. R.L. Fleischer: in *The Strengthening of Metals,* D. Peckner, ed., Reinhold Publishing Corporation, London, 1964, pp. 93-140.
23. J. Menzel, W. Kirschner, and G. Stein: *Iron Steel Inst. Jpn. Int.,* 1996, vol. 36, pp. 893-900.
24. P.J. Uggowitzer, R. Magdowski, and M.O. Speidel: *Iron Steel Inst. Jpn. Int.,* 1996, vol. 36, pp. 901-08.
25. E.V. Kozlov, N.A. Koneva, A.V. Plevkov, and T.V. Cherkasova: *Materials Science Forum,* Trans Tech Publications, Uetikon-Zuerich, 1999, vols. 318-320, pp. 461-65.
26. R. Labusch: *Phys. Status Solidi,* 1970, vol. 41, pp. 659-69.
27. J.J. Romu, J.J. Tervo, H.E. Hanninen, and J. Liimatainen: *Iron Steel Inst. Jpn. Int.,* 1996, vol. 36, pp. 938-46.
28. V.G. Gavriljuk and H. Berns: *High Nitrogen Steels—Structure, Properties, Manufacture, Applications,* Springer, Berlin, 1999, pp. 213-15.