Performing the solution nitriding treatment under pressurized nitrogen gas atmosphere, the microstructure change and the relationship between the nitrogen gas pressure and the solute nitrogen content in Fe–Cr alloys were investigated. The microstructure of the ferritic Fe–Cr alloys changed to an austenitic structure by the pressurized solution nitriding treatment at 1 473 and 1 573 K. However, in the case that their martensite temperature did not decrease sufficiently lower than room temperature, martensitic transformation occurred during the cooling process. Examination of the interaction on nitrogen activity with the thermodynamic method confirmed that the deviation between the experimental and theoretical solute nitrogen contents in Fe–Cr alloys widened greatly in the high nitrogen region over 3 at% N because of the strong N–N interaction in austenite. The interaction parameter $e_{\text{Ni}}^{[\text{N}]}$ between N atoms in austenite iron at 1 473 K was obtained as 0.120. The temperature dependence of $e_{\text{Ni}}^{[\text{N}]}$ is expressed as follows:

$$e_{\text{Ni}}^{[\text{N}]} = \frac{217}{T} - 0.0273$$

KEY WORDS: Ni-free austenitic stainless steel; high nitrogen steels; pressurized solution nitriding treatment; nitrogen absorption treatment; interaction parameter.

1. Introduction

In the field of surgical and dental implant materials, non-magnetic austenitic stainless steels are mainly used in order to avoid the influence on tomographic images of tissue using magnetic resonance imaging (MRI). However, since nickel in those materials, such as in SUS304 and SUS316 stainless steels, is considered to cause allergies, many researchers are recently interested in the development of Ni-free austenitic stainless steels.1–7)

Like nickel, nitrogen is a strong austenite stabilizer. The effect of the addition of N to iron and steel has been investigated in order to improve the material properties. For example, in austenitic stainless steels, the strength of the steels can be greatly increased without excessive lowering of ductility and corrosion resistance, especially pitting corrosion resistance, is improved. However, in consideration of the harmful influence of sensitization such as intergranular corrosion and stress-corrosion, commercial steels contain only about 0.5% N at maximum. On the other hand, since the new austenitic stainless Fe–Cr–N-based alloys with 1% solute nitrogen instead of Ni have higher strength and higher corrosion resistance than usual austenitic stainless steels, the development of the Ni-free high nitrogen stainless steels has attracted attention. The introduction of N in steels can be performed by high-pressurized nitrogen electro-slag remelting (ESR) method,2,3) nitrogen absorption treatment4,5) and mechanical alloying (MA) treatment.7) Nitrogen absorption treatment, in other words, the solution nitriding (SN) treatment we used in the present study is solid-solution treatment under N$_2$ atmosphere for the steel surface or the entire steel. The advantage of SN treatment as compared with other methods is the secondary process after the mechanical work of the ferritic Fe–Cr based alloys, which have lower work hardening and better formability than the austenitic alloys with N. However, since SN treatment requires a long time for the diffusion of N into steels, it is difficult to apply to a practical steel-making process at the present time. Moreover, although SN treatment under 0.1 MPa N$_2$ gas has been investigated but there are few report of the N$_2$ gas pressure dependence on the solute N content in Fe–Cr alloys SN-treated under pressurized N$_2$ gas.

Thus, in the present study, using pressurized SN treatment, the microstructure change and the relationship between N$_2$ gas pressure and solute N content in Fe–Cr alloys were investigated.

2. Experimental

SUS430 stainless steel (Fe–16%Cr) and Fe–(7, 20, 24)%Cr alloys were used. Ingots with 35 g of Fe–(7, 20, 24)%Cr alloys were prepared by arc melting in an argon gas atmosphere. The specimens were hot-rolled at 1 273 K to a thickness of 3.0 mm and then cold-rolled to a thickness of 1.0 mm after removal of the surface scale. Table 1 shows the chemical composition of the specimen materials. Pressurized SN treatment was performed by a high vacuum heat treatment instrument which is also able to be

| Table 1 | Chemical Composition of Specimen Materials |
|---------|------------------------------------------|
| Alloy   | Fe | Cr | N |
| 7%     | 94 | 6  | 0.5 |
| 20%    | 80 | 20 | 1  |
| 24%    | 76 | 24 | 1.5|

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pressurized up to 0.7 MPa. After evacuation and elevation of the temperature to 1473 and 1573 K at 10 K/min, the specimens were equilibrated in a nitrogen gas atmosphere at 0.1, 0.2, 0.4 and 0.7 MPa. The equilibrating times of 1473 K/H11003 8h  and 1573 K/H11003 4h  were based on the pre-experiment. The rate of gas cooling (0.7 MPa) to 773 K was about 100 K/s and it took 5 min to reach room temperature.

Microstructure examination was carried out with an optical microscope (OM). The mirror-polished sections of the specimens for OM observations were etched in a Villela reagent or electrically etched in a 10% oxalic acid.

3. Results and Discussion

3.1. Microstructure Change by Pressurized SN Treatment

Figure 1 shows micrographs of Fe–16%Cr and Fe–24%Cr alloys pressurized-SN treated at 1473 K for 8 h under 0.1 MPa N2 (left) and 0.7 MPa N2 (right). (a) Fe–16%Cr–0.43%N, (b) Fe–16%Cr–0.86%N, (c) Fe–24%Cr–1.10%N, (d) Fe–24%Cr–1.82%N (mass%).

![Micrographs](image)

Table 1. Chemical composition.

|        | C    | Si   | Mn   | P    | S    | Ni   | Cr   | Mo   | Fe   |
|--------|------|------|------|------|------|------|------|------|------|
| SUS430(Fe–16%Cr) | 0.06 | 0.39 | 0.77 | 0.028 | 0.006 | 0.14 | 16.21 | 0.014 | bal. |
| Fe–7%Cr | <0.01 | 0.045 | <0.01 | <0.01 | 0.001 | <0.01 | 6.50  | <0.01 | bal. |
| Fe–20%Cr | <0.01 | 0.042 | <0.01 | <0.01 | 0.002 | <0.01 | 20.20 | <0.01 | bal. |
| Fe–24%Cr | <0.01 | 0.049 | <0.01 | <0.01 | 0.001 | <0.01 | 24.05 | <0.01 | bal. |

where the effect of N on the change of the $M_S$ point is added to Eq. (1), assuming the same tendency as that of C, which has a similar atomic radius. Since the calculated $M_S$ point of Fe–16%Cr–0.43%N alloy is 349 K, it is considered that the microstructure was transformed from the γ phase to the M phase during cooling. Fe–16%Cr–0.86%N and Fe–24%Cr–1.10%N alloys have the γ phase in the matrix, as shown in Figs. 1(b) and 1(c), respectively. On the other hand, as shown in Fig. 1(d), lamellar nitrides as well as the γ phase in the matrix are observed in Fe–24%Cr–1.82%N alloy. This is similar to the pearlite microstructure by eutectoid transformation, $\gamma \rightarrow \alpha + Fe_3C$, in the Fe–C system. As shown in Fig. 3, the calculated vertical section phase diagram of the Fe–24%Cr–(0–2.5)%N system suggests the possibility of the transformation from $\gamma$ to $\alpha +$ nitride in the region of 1.0–2.5% N. Zener explained that the rate of the pearlite reaction, $G$, which is closely related to the driving force of the reaction, depends on the degree of supersatura-

![Graph](image)

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tion as shown in the following equation.\(^9\)

\[
G = 2 \left( \frac{x^c - x^e}{x^c} \right) \frac{D}{l} \tag{2}
\]

where \(x^c\) and \(x^e\) are the supersaturated and the equilibrium solute contents, respectively, \(l\) is the interval of layers and \(D\) is the diffusion coefficient. Furthermore, since the calculated mole fraction of Cr\(_2\)N in Fe–24%Cr–1.82%N at 1 000 and 1 100 K is higher than that of Fe–24%Cr–1.10%N, as shown in Table 2, it is considered that the former alloy easily occurs eutectoid transformation. In general, the cooling rate of water and air is about 1 000 K/s and 1 K/s, respectively, while that in this study was about 100 K/s in the high temperature region between 1 473 and 773 K; this is comparatively slower than so-called rapid cooling. Therefore, it is considered that the lamellar nitrides observed in the Fe–24%Cr–1.82%N alloy precipitated during cooling.

Figure 4 shows micrographs of Fe–16%Cr and Fe–24%Cr alloys pressurized-SN treated at 1 573 K for 4 h at 0.1 and 0.7 MPa. Both Fe–16%Cr–0.35%N (Fig. 4(a)) and Fe–16%Cr–0.66%N (Fig. 4(b)) alloys have a martensitic microstructure, which can be examined by the estimation of the \(M_S\) point with Eq. (1) in the same way as in Fig. 1(a). On the other hand, the microstructure of the Fe–24%Cr–0.22%N alloy is in the \(\alpha + \gamma\) dual-phase as shown in Fig. 4(c). This result agrees with the calculated isothermal phase diagram of the Fe–Cr–N ternary system at 1 573 K (Fig. 2(b)). As shown in Fig. 4(d), Fe–24%Cr–1.31%N alloy is in the \(g\) single phase.

3.2. Relationship between \(N_2\) Gas Pressure and Solute N Content

The equilibrium between \(N_2\) gas pressure and solute N content in an Fe–Cr alloy is represented by Eq. (3), namely, Sievert’s law:

\[
N_2 (\gamma - Fe) = \frac{1}{2} N_2 \quad \alpha = a_N / \sqrt{P_{N_2}} \quad K' = [\%N] / \sqrt{P_{N_2}}
\]

where \(K\) and \(K'\) are, respectively, the ideal and the proportional equilibrium constants. The activity \(a_N\) is given by the activity coefficient \(f_N\) and the measured N content \([\%N]\) as the following equations:

\[
\log a_N = \log f_N + e_N^{[Cr]} [\%Cr] + e_N^{[C]} [\%C] + e_N^{[Mn]} [\%Mn] + r_N^{[Mn]} [\%Mn]^2 + w_N^{[Cr,Mn]} [\%Cr][\%Mn] \tag{5}
\]

where \(e_N^{[X]}\), \(r_N^{[X]}\) and \(w_N^{[X,Y]}\) are the interaction parameters of \(X\) (and \(Y\)) on N in austenitic iron. In this study, since Mn has a large influence on the solution of N in steel while the effect of the other minor elements can be ignored because of \(e_N^{[X]}[\%X]=0\), the third term and subsequent terms of Eq. (5) were included in the calculation of \(f_N\) in the SUS430 stainless steel. Thus, the relationship between \(K\) and \(K'\) is expressed as follows:

\[
\log K = \log K' + e_N^{[Cr]} [\%Cr] + r_N^{[Cr]} [\%Cr]^2 + e_N^{[Mn]} [\%Mn] + r_N^{[Mn]} [\%Mn]^2 + e_N^{[Cr,Mn]} [\%Cr][\%Mn] \tag{6}
\]

\[
\log [\%N] = \log [\sqrt{P_{N_2}}] + \log K - e_N^{[Cr]} [\%Cr] - r_N^{[Cr]} [\%Cr]^2 - e_N^{[Mn]} [\%Mn] - r_N^{[Mn]} [\%Mn]^2 - e_N^{[Cr,Mn]} [\%Cr][\%Mn] \tag{7}
\]

Table 2. Calculated mole fractions of \(\alpha\) and Cr\(_2\)N in Fe–24%Cr–1.10%N and Fe–24%Cr–1.82%N alloys at 1 000 and 1 100 K.

| Temp.     | Fe–24%Cr–1.10%N | Fe–24%Cr–1.82%N |
|-----------|----------------|-----------------|
| 1000 K    | 0.8724         | 0.1276          |
| 1100 K    | 0.8723         | 0.1277          |
Figure 5 and Table 3 show the relationship between N$_2$ gas pressure and solute N content in equilibrium at 1473 and 1573 K. The broken line in Fig. 5(a) was calculated by Eq. (7). The value of $K$ (Eq. (8)) is equal to that of the Fe–N binary system reported by Mori et al.\textsuperscript{10)}

$$\log K = \frac{652}{T} - 2.093$$

$$\log K (1473 K) = -1.650, \quad \log K (1573 K) = -1.678 \ldots \text{(8)}$$

The interaction parameters at 1473 K, as shown in Table 3, are the same as those of Tsuchiyama et al. The measured N content at 1473 K is lower than the calculated one. This is the same tendency as the result of the Fe–N system by Masumoto et al.\textsuperscript{13)}; i.e., the N content absorbed under high-pressurized N$_2$ gas does not agree with Sievert's
law. It is considered that the result at 1 573 K is the same tendency because the extrapolation line of N content toward $P_N^N \rightarrow 0$ does not pass through the origin.

3.3. Interaction between N Atoms in the g Phase

With a content above 3 at% N in the Fe–Cr alloys as shown in Fig. 6, the experimentally measured N content does not wholly agree with the theoretical one calculated by Eq. (7). In past studies, the difference from Sievert’s law in high N alloys was considered to be caused by the interaction between solute N atoms. Masumoto et al. postulated that one N atom, assuming that a face-centered cubic of austenite iron has octahedral interstitial positions, excludes the first and the second neighbors because of the N–N repulsive interaction, i.e., the nearest neighbor N atoms are arranged at each central octahedral point of every second unit cell as shown in Fig. 7(a). The N content when N atoms are positioned in all of the solid rounds is 12 at% (about 3 mass%), which agrees with the maximum solubility of N in austenite iron. Therefore, the group of unit cells involved in the strong N–N interaction is the gray region in Fig. 7(a), namely Fig. 7(b). The minimum N content, 3 at% (about 0.7 mass%), agrees well with the beginning of the large difference from Sievert’s law, as shown in Fig. 6. Taking into account the effect of the N–N interaction, Eqs. (5)–(7) are modified as follows:

$$\log f_N = e_N^{[N]}[\%N] + e_N^{[Cr]}[\%Cr] + r_N^{[Cr]}[\%Cr]^2 + e_N^{[Mn]}[\%Mn] + r_N^{[Mn]}[\%Mn]^2 + w_N^{[Cr,Mn]}[\%Cr][\%Mn]$$

(9)

$$\log K = \log K' + e_N^{[N]}[\%N] + e_N^{[Cr]}[\%Cr] + r_N^{[Cr]}[\%Cr]^2 + e_N^{[Mn]}[\%Mn] + r_N^{[Mn]}[\%Mn]^2 + e_N^{[Cr,Mn]}[\%Cr][\%Mn]$$

(10)

Considering that the contribution of the N–N interaction changes remarkably in the border of 0.7 mass% N, fundamentally, a quadratic term, $e_N^{[N]}[\%N]^2$, should be added to Eqs. (9)–(11). However, we used only a linear term, $e_N^{[N]}[\%N]$, for the sake of simplicity.

The relationship between log $K$ by Eq. (10) and solute nitrogen content in Fe–Cr alloys at 1 473 K is shown in Fig. 8. The value of $e_N^{[N]}$ at 1 473 K is obtained as 0.120 from the slope of the approximate equation with an intercept of $-1.650$ (Eq. (8)) by the method of least squares. This is slightly larger than the interaction parameter of C on N in $\gamma$-Fe, $e_N^{[Cr]}=0.085$. As shown in Fig. 9, the theoretical nitrogen content by Eq. (11) agrees well with the experimentally measured one.

Figure 10(a) shows the relationship between solute N content and N$_2$ gas pressure reported by Masumoto et al. The values of $e_N^{[N]}$ in austenite iron at 1 223 and 1 273 K are recalculated as 0.150 and 0.143, respectively. The obtained temperature dependence of $e_N^{[N]}$ is shown in Fig. 10(b) and Eq. (12).

$$e_N^{[N]} = \frac{217}{t} - 0.0273 \quad \cdots \quad (12)$$
3.4 Interaction Parameter of Cr on N in Austenite at 1573 K

The relationship between Cr content and \( \log K' + e_N^{[N]} \%N \) is expressed by Eq. (10) as the quadratic function of \( \%Cr \) with the intercept of \( \log K \). Figure 11 shows the relationship between Cr content and \( \log K' + e_N^{[N]} \%N \) at 1473 and 1573 K. The theoretical curve at 1473 K, viz., the value of the 3rd term and after that of Eq. (10), agrees with the results by Tsuchiyama et al., which are not used for the calculation of \( e_N^{[N]} \) in this study. The values of \( \log K \) and \( e_N^{[N]} \) at 1573 K are \(-9.08 \times 10^{-2}\) and \(1.07 \times 10^{-3}\), respectively, provided that the results of Fe–20%Cr and Fe–24%Cr at 0.1 MPa N₂ gas are excluded from the calculation because they are not single austenite.

4. Summary

In this study, performing solution nitriding treatment under pressurized nitrogen gas atmosphere, the microstructure change and the relationship between nitrogen gas pressure and solute nitrogen content in Fe–Cr alloys were investigated. The results obtained were as follows:

(1) The microstructure of the ferritic Fe–Cr alloys changed to austenite by the solution nitriding treatment at 1473 and 1573 K. However, in the case that their martensitic temperature did not decrease sufficiently lower than room temperature, martensitic transformation occurred during the cooling process.

(2) It was confirmed that the deviation between the experimental and theoretical solute nitrogen contents in Fe–Cr alloys widened greatly in the high nitrogen region over 3 at% N because of the strong N–N interaction in austenite.

(3) The interaction parameter \( e_N^{[N]} \) between N atoms in austenite iron at 1473 K was obtained as 0.120. The temperature dependence of \( e_N^{[N]} \) is expressed as follows:

\[
e_N^{[N]} = \frac{217}{T} - 0.0273
\]

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