1. Introduction

Nitriding of stainless steels has attracted much attention in the pursuit of developing materials having high wear and corrosion resistance. Since the surface properties of the nitrided steels are affected significantly by the formation of nitrides, control of the nitride precipitation is required for obtaining desirable properties.

Several studies have been conducted on nitride precipitation in Fe–Cr ferritic alloys during nitriding. Philips and Seybolt\(^1\) reported that fine disk-shaped CrN forms by continuous precipitation in ferrite (\(\alpha\)) matrix in an Fe–1 mass\%Cr (hereafter composition is expressed in terms of mass\%) alloy plasma-nitrided at 823 K. Furthermore, Schacherl\(^2\) et al. reported that the nitrided zone in the Fe–4\%Cr and Fe–7\%Cr specimens gaseous-nitrided at 843 K is composed of two different regions; one consists of ferrite (\(\alpha\)) grains containing fine dispersion of CrN and the other consists of (\(\alpha+\)CrN) lamellar structure. Recently, the present authors\(^3\) investigated the microstructure of Fe–18\%Cr alloy plasma-nitrided at temperatures ranging from 743 to 943 K. They found that the entire nitrided zone is composed of (\(\alpha+\)CrN) lamellar structure at 743 and 843 K, whereas disk-shaped CrN and small amounts of rod-shaped CrN and Cr,N form in the \(\alpha\) matrix by continuous precipitation at 943 K. Thus, the nitriding behavior of Fe–Cr alloys is clearly significantly affected by the Cr content as well as the nitriding temperature. However, no systematic study has been conducted on the nitriding behavior in Fe–Cr alloys over a wide range of Cr content.

In the present study, microstructure and growth kinetics of the nitrided zone have been investigated in the plasma-nitrided Fe–Cr alloys containing 1 to 30 mass\% Cr.

2. Experimental Procedure

2.1. Material Preparation

Fe–Cr binary alloys containing 0.94, 2.86, 9.69, 18.4, and 30.2\% Cr (hereafter these are denoted by Fe–1\%Cr, Fe–3\%Cr, Fe–10\%Cr, Fe–18\%Cr, and Fe–30\%Cr alloys, respectively) were used. The Fe–18\%Cr alloy was prepared by vacuum melting, and the other alloys were prepared by arc melting. The Fe–1\%Cr, Fe–3\%Cr, and Fe–10\%Cr alloys were homogenized at 1 453 K for 86.4 ks and subsequently air-cooled to room temperature. These specimens were annealed again at 1 073 K for 18 ks to remove dislocations introduced during the transformation from austenite to ferrite during the course of cooling. The Fe–1\%Cr and Fe–3\%Cr alloys were homogenized at 1 453 K for 86.4 ks and subsequently air-cooled to room temperature. These specimens were annealed again at 1 073 K for 18 ks to remove dislocations introduced by the transformation from austenite to ferrite during the course of air cooling. The Fe–18\%Cr and Fe–30\%Cr alloys were quenched in water following the same homogenization process. Cubic specimens of 5\(\times\)5\(\times\)5 mm\(^3\) were cut from these heat-treated specimens, and their surfaces were mechanically polished and cleaned in acetone before nitriding.

2.2. Plasma-nitriding

The specimen surface was first sputtered for cleaning in a gas mixture of 50%H\(_2–50\%Ar\) at a nitriding temperature for 3.6 ks in a nitriding furnace. Subsequently, the plasma nitriding process was carried out at temperatures ranging from 743 to 943 K for various periods in a gas mixture of...
20%N₂–80%H₂ (total pressure was 700 Pa) and cooled in the furnace. Nitriding temperatures were controlled by monitoring the temperature of a dummy sample to which a thermocouple was attached. The difference between the monitored and the actual temperatures was corrected while the eutectoid temperature in the Fe–N binary system (863 K) was used as a reference.

2.3. Metallographic Observation and Hardness Measurement

Microstructure observation was carried out by means of optical microscopy (OM), scanning electron microscopy (SEM: JSM-6500F operated at 15 kV), and transmission electron microscopy (TEM: CM-200FEG operated at 200 kV). The nitrided specimens were prepared for OM and SEM observations by mechanically polishing after they had been Ni electroplated to protect the edges of the specimens during polishing. A 5% nital solution was used for etching of the Fe–1%Cr and Fe–3%Cr specimens, and the Fe–10%Cr, Fe–18%Cr and Fe–30%Cr specimens were subjected to electroetching at 22 V in a solution of 450 mL CH₃COOH, 50 mL HClO₄ acid. Thin foil specimens for TEM observation were prepared either by ion milling or by twin jet electropolishing at 33 V in a solution of 500 mL CH₃COOH, 20 mL H₂O, and 100 g CrO₃ at 283 K. The hardness distributions in the nitrided specimens were measured by a micro-indentation tester equipped with a Berkovich indenter, under a load of 49 mN. The hardness was expressed as universal hardness (HU), which was calculated from the load and indentation displacement. The thickness of the nitrided zone is estimated from the hardness–depth profile as the distance between the surface and the point where the increase in hardness from the unnitrided zone is 20% of the largest increase. Furthermore, to determine the phase after nitriding, X-ray diffraction (XRD) experiments were performed with Cu Kα radiation. After repeated polishing, the XRD patterns were recorded at various depths from the surface.

3. Results and Discussion

3.1. Hardness–Depth Profile and Microstructure in Plasma-nitrided Fe–Cr Specimens

Figure 1 shows the hardness–depth profiles of the nitrided specimens. As shown in Fig. 1(a), in the Fe–3%Cr specimens nitrided at 843 K, hardness decreases gradually with increasing depth from the surface. When Cr content is increased to 18%, at the same nitriding temperature, hardness in the nitrided zone increases and the thickness of the nitrided zone decreases (Fig. 1(b)). In the Fe–18%Cr specimen nitrided at 943 K shown in Fig. 1(c), hardness is almost constant in the nitrided zone and decreases sharply at the growth front of the nitrided zone.

Figure 2(a) shows a cross-sectional OM image of the Fe–3%Cr specimen nitrided at 843 K for 18 ks, and Fig. 2(b) shows a cross-sectional SEM image of a cross-section in the Fe–18%Cr specimen nitrided at 943 K for 18 ks.
gated parallel to the direction of nitriding. Furthermore, the
enlarged image of the growth front shown in Fig. 3(b) indi-
cates that the nitrided zone consists of a lamellar structure,
as has been reported previously.3)

Figures 4(a) and 4(b) show XRD patterns obtained at
various depths from the surface of the Fe–18\%Cr speci-
mens nitrided at 843 K and 943 K for 18 ks, respectively.
These XRD patterns reveal the presence of bcc \( \alpha \) and \( \text{CrN} \)
in the entire nitrided zone under these nitriding conditions.
In addition, a small amount of fcc \( \gamma'\text{-M}_2\text{N} \) is detected near
the specimen surface. Under both sets of conditions, the in-

Fig. 3. (a) SEM image of a cross-section in the Fe–18\%Cr speci-
men nitrided at 843 K for 18 ks, (b) enlarged image near
the growth front of the nitrided zone in (a).

Fig. 4. XRD patterns recorded from various depths from the sur-
face of the Fe–18\%Cr specimen nitrided at (a) 843 K for
18 ks, (b) 943 K for 18 ks.

Fig. 5. Various Cr–nitrides formed in the nitrided zone of the Fe–Cr alloys, (a) the Fe–3\%Cr specimen nitrided at 943 K
for 18 ks, (b) the Fe–18\%Cr specimen nitrided at 943 K for 18 ks at a depth between 40–60 \( \mu \)m from the surface,
(c) the Fe–18\%Cr specimen nitrided at 943 K for 18 ks at a depth between 90–130 \( \mu \)m, which is close to the
growth front of the nitrided zone, (d) the Fe–18\%Cr specimen nitrided at 843 K for 18 ks.
tensity of CrN peaks decreases gradually with increasing depth from the surface.

The microstructure of the nitrided specimens was observed in detail by TEM to clarify the precipitates formed in the nitrided zone. Figure 5 shows observed TEM microstructure in the Fe–3%Cr specimen (Fig. 5(a)), along with those of the Fe–18%Cr specimens reported in the previous study (Figs. 5(b)–5(d)). Disk-shaped CrN precipitates form having (001)_{α}/(001)_{CrN} as a habit plane in the Fe–3%Cr specimen nitrided at 943 K (Fig. 5(a)). Although (α+CrN) lamellae were observed in part of the nitrided zone of the Fe–3%Cr alloy gaseous-nitrided at 823 K, in this study the lamellar structure does not form in the Fe–3%Cr specimens plasma-nitrided at the temperatures ranging from 743 to 943 K. In the Fe–18%Cr specimen nitrided at 943 K shown in Fig. 5(b), disk-shaped CrN precipitates are observed in most of the nitrided zone. However, in the region close to the growth front of the same specimen, only Cr2N forms (Fig. 5(c)), because Cr2N is more stable than CrN at lower N concentration. Therefore, as reported previously, the increase in N concentration during nitriding causes a transformation from Cr2N to CrN. Meanwhile, the entire nitrided zone in the Fe–18%Cr specimen nitrided at 843 K exhibits the (α+CrN) lamellar structure (Fig. 5(d)).

Figures 6(a) and 6(b) show SEM images of the Fe–18%Cr specimen nitrided at 843 K for 72 ks, which are observed along the normal direction to the specimen surface at depths of 2 μm and 87 μm from the specimen surface, respectively. The interlamellar spacing of (α+CrN) lamellae increases with depth, from approximately 25 nm (Fig. 6(a)) to 50 nm (Fig. 6(b)). Figure 6(c) shows the interlamellar spacing as a function of distance from the surface in the Fe–18%Cr specimens nitrided under various conditions. The interlamellar spacing increases with increasing nitriding temperature. The change in interlamellar spacing with depth is small at 743 K, whereas the spacing increases significantly with depth at 843 K and 893 K.

Figure 7 summarizes Cr–nitrides identified in the Fe–(1–18)%Cr alloys nitrided at 843 and 943 K in this study. At 943 K, the disk-shaped CrN forms through continuous precipitation in the α matrix in all the specimens, and furthermore, small amounts of Cr2N are observed in the Fe–18%Cr specimen. Whereas the disk-shaped CrN forms in the α matrix in the lower Cr specimens at 843 K, the entire nitrided zone in the Fe–10%Cr and Fe–18%Cr specimens consists of (α+CrN) lamellar structure at this temperature. Hence, CrN forms at higher temperature and higher Cr content. Such tendency coincides well with that reported by Mortimer et al. in gaseous-nitriding of Fe–Cr alloys. Furthermore, at higher Cr content and lower nitriding temperature, (α+CrN) lamellar structure tends to form. The present authors have clarified that the orientation of α in the lamellar structure differs greatly from that of the original α grains. According to a proposed mechanism, recrystallization of α is induced by continuous precipitation of CrN due to volumetric mismatch between CrN and the α matrix, and subsequent discontinuous precipitation at the grain boundary between the recrystallized and original α grain forms the (α+CrN) lamellar structure. Thus, we conclude that precipitation behavior of Cr–nitrides in nitriding of Fe–Cr alloys changes drastically with Cr content and nitriding temperature.
3.2. Growth Kinetics of the Nitrided Zone in Nitriding of Fe–Cr Alloys

In Fig. 8, the squares of the nitrided zone thickness ($L^2$) of the Fe–3%Cr and Fe–18%Cr specimens nitrided at various temperatures are plotted as a function of nitriding period ($t$). Under all nitriding conditions, $L^2$ is approximately proportional to $t$ (Figs. 8(a) and 8(b)), indicating that the growth of the nitrided zone is diffusion-controlled. At a higher nitriding temperature or a lower Cr content, the nitrided zone grows faster. Linear relationships were also observed between $L^2$ and $t$ in the other Fe–(1, 10, 30)%Cr specimens nitrided at all the temperatures investigated. Hence, the square of the nitrided zone thickness can be described by the following equation:

$$L^2 = K \cdot t \..................................(1)$$

where $K$ is a growth constant of the nitrided zone. $K$ values for all the specimens were obtained by least square fit of the experimental data to Eq. (1). Figure 9 shows Arrhenius plots of $K$ against the inverse of nitriding temperature ($T$). Figure 9 indicates that, for each alloy, the plot of the $K$ value is approximately aligned on a single straight line. Furthermore, the slopes of the lines are nearly the same for all the alloys in spite of the remarkable difference in the morphologies of Cr–nitrides. The decrease in growth rate with increasing nitriding temperature as reported by Granito et al. is not observed in this study. Table 1 shows the activation energy ($Q$) and pre-exponential factor ($K^*$) in each alloy as estimated by the following equation:

$$K = K^* \cdot \exp(-Q/RT) \...........................(2)$$

where $R$ is the gas constant. The $K^*$ value decreases with increasing Cr content, whereas the change in the $Q$ value with Cr content is not large. These $Q$ values are closer to that for bulk diffusion of N (79.1 kJ/mol) than to that for bulk diffusion of Cr (238.8 kJ/mol) in $\alpha$. This indicates that the growth of the nitrided zone is mainly controlled by the diffusion of N in the $\alpha$ matrix if most of the temperature dependence of $K$ is attributed to diffusion process.

The internal oxidation theory proposed by Wagner has been frequently applied to interpret the kinetics in nitriding of Fe–Cr alloys while assuming the following conditions.

1) Inward diffusion of N is a rate-controlling process, and macroscopic diffusion of Cr is negligible.

2) Diffusing N atoms are immediately bound to Cr atoms that dissolve in the $\alpha$ matrix, resulting in a sharp boundary between the nitrided and unnitrided zones. The observed kinetics and microstructure correspond fairly well to this theory. According to Wagner’s theory, $K$ in Eq. (1) is approximately described as

$$K = 2 \cdot C_N \cdot D_N/(vC_C) \...........................(3)$$

where $C_N$ is N concentration in $\alpha$ at the specimen surface, $D_N$ is the diffusion coefficient of N in $\alpha$, and $C_C$ is the mole fraction of Cr content in the specimen. $v$ represents the atomic ratio of N to Cr in nitrides. $C_N$ is usually assumed to be equal to the N concentration in $\alpha$ equilibrated.
with the external nitrided layer. Thus, in nitriding of low-alloyed steels, $C_N$ has been taken to be the solubility in $\alpha$ equilibrated with Fe$_2$N in the Fe–N binary system.\(^{10,11}\) However, uncertainty remains as to whether this assumption is also valid for the nitriding of high-Cr steels, since the equilibrium concentration of N depends on Cr content. Hence, $C_N$, estimated by substituting $K$ into Eq. (3), denoted as $C_N^{\exp}$, is compared with the N solubility in the Fe–N binary system.

Here $D_N$ in pure iron\(^7\) is used, because the solubility limit of Cr in $\alpha$ with respect to CrN is much small in the nitriding temperatures used in this study.\(^{12}\) $\nu$ is assumed to be unity for all the alloys at all the nitriding temperatures, because in most cases the nitrides observed in the nitrided zone are CrN. Figure 10 compares values of $C_N^{\exp}$ with the solubility limit of N calculated by ThermoCalc in the Fe–N binary system. In view that the phases equilibrated with $\alpha$ in the Fe–N binary system are Fe$_2$N below the eutectoid temperature; i.e., 863 K, and austenite ($\gamma$) above this temperature, the concentrations of N in $\alpha$ equilibrated with Fe$_2$N and $\gamma$ are illustrated as a dashed line and a solid line, respectively, in Fig. 10. The formation of $\gamma$ was observed near the specimen surface in the Fe–1%Cr and Fe–3%Cr specimens nitrided at 943 K, and $\gamma$ did not appear under the other nitriding conditions. As shown in Fig. 10, $C_N^{\exp}$ for the Fe–3%Cr and Fe–10%Cr specimens are close to the solubility of N in the Fe–N binary system. On the other hand, $C_N^{\exp}$ of the Fe–18%Cr and Fe–30%Cr specimens are nearly constant with temperature and deviates largely from the solubility limit of N in the binary Fe–N system. Hence, we conclude that an increase in the Cr content results in a significant decrease in $C_N$. This is because the external nitriding layer composed of (Fe,Cr)$_2$N is stabilized thermodynamically by dissolving Cr,\(^{13,14}\) resulting in a drop in the N concentration in $\alpha$ equilibrated to the external nitriding layer. However, due to lack of information of N potential in plasma nitriding, further discussion of the effect of Cr content on $C_N$ is difficult.

Thus, we conclude that the $C_N$ dependence on the Cr content should be taken into account to interpret the growth kinetics of the nitrided zone in high-Cr steels by applying Wagner’s theory.

4. Summary

Microstructure and growth kinetics of the nitrided zone were investigated in Fe–(1–30)mass%Cr binary alloys that had been plasma-nitrided at temperatures ranging from 743 to 943 K. The results obtained are summarized as follows.

(1) Disk-shaped CrN forms through continuous precipitation in the $\alpha$ matrix in the Fe–(1, 3, 10, 18)%Cr alloys nitrided at 943 K. In addition to the CrN, Cr$_2$N is observed near the growth front of the Fe–18%Cr alloy nitrided at the same temperature. The disk-shaped CrN also forms in the Fe–(1, 3)%Cr alloys nitrided at 843 K.

(2) The nitrided zones in the Fe–(10, 18)%Cr alloys nitrided at temperatures below 843 K consist of ($\alpha$+CrN) lamellar structure. The interlamellar spacing of ($\alpha$+CrN) decreases with decreasing the temperature and increasing depth from the specimen surface.

(3) In all the alloys and at all temperatures, the square of the thickness of the nitrided zone is nearly proportional to the nitriding period. We conclude that growth of nitrided zone is nearly controlled by N diffusion in $\alpha$, regardless of differences in precipitate morphology.

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