Formation of Austenite and Martensite in the Surface Layer of Pure Iron with Ion-Nitriding*

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Pure iron was ion-nitrided in a mixed gas (80 vol% N_2 + 20 vol% H_2) under a reduced pressure of 665 Pa at 803, 923 and 1013 K and then quenched in water for the elucidation of the ion-nitriding behavior accompanied with phase transformations above the eutectoid transformation temperature of 863 K for the Fe-N system.

When nitrided at 803 K, the nitrided specimen surface consists of two layers as usual nitrided cases do; (i) a compound layer with a hardness of about Hv 700 which is mainly composed of γ' -Fe₄N, and (ii) a diffusion layer of about Hv 250.

When nitrided at 923 K, the nitrided specimen surface consists of; (i) a compound layer of about Hv 750, mainly composed of γ' -Fe₄N, under which are (ii) an inner layer of γ austenite of about Hv 400 and (iii) a diffusion layer.

When nitrided at 1013 K, the nitrided specimen surface consists of; (i) a thin compound layer, (ii) an inner hardened layer of γ and α' martensite, of which the hardness increases from Hv 400 to Hv 700 toward the inside corresponding to the content of the α' phase, and (iii) a diffusion layer.

To explain the formation of the relatively thick hardened layers of austenite at 923 K and martensite at 1013 K, the nitrogen concentration at each temperature and the degree of the stability of the γ phase when quenched in water after nitriding were examined.

(Received June 6, 1991)

Keywords: ion-nitriding, pure iron, nitrided case, phase transformation, austenite, martensite, compound layer, diffusion layer

I. Introduction

The ion-nitriding⁽¹⁾⁻⁽¹²⁾ is one of the methods for the surface hardening of steels, carried out in a N_2 - H_2 glow discharge plasma. This treatment has many advantages compared with other nitriding methods, and has been developed to improve resistivity to wear, fatigue and corrosion of ferrous engineering components. Though this treatment has widely been used and the properties practically important such as the hardness have been investigated minutely, the mechanism of the formation of nitrided layer has not been elucidated yet in detail. Under the restrictions of avoiding the occurrence of phase transformation in parent materials, most of experimental work to improve the nitriding rate constant and surface hardness of steels has been carried out at temperatures ranging from 773 to 873 K. For example, the authors⁽¹²⁾ have obtained the nitrided layer with a high hardness and a high corrosion resistivity of type 304 austenitic stainless steel applying the low temperature of about 623 K to ion-nitriding. It is expected, therefore, that the ion-nitriding out of the temperature range described above will yield interesting results.

The solubility of nitrogen in iron is larger than that of carbon and the A_3 temperature of the Fe-N phase diagram is lowered considerably by the addition of nitrogen. The extent of lowering the A_3 temperature is very large in the Fe-N phase diagram compared with the

A_3 temperature of the Fe-C phase diagram. And it is well-known that the eutectoid transformation temperature, at which the reaction of γ -Fe $\rightarrow$ α -Fe + γ' -Fe₄N occurs, is 863 K at 2.35 mass%N⁽¹³⁾, while in the Fe-C diagram it is 996 K at 0.8 mass%C. Based on the above consideration, austenite and martensite are generated in the surface layer without the phase transformation of the parent material for the low carbon steel by the ion-nitriding at a temperature between 863 and 996 K.

In the present paper, to elucidate the mechanism of the ion-nitriding and the phase transformations in the nitrided surface layer, pure iron was selected to study for its familiarity of the phase diagram and its physical properties. By means of an X-ray diffractometer, an optical microscope, SEM, EPMA and a micro-vickers hardness tester, the nitrided layers were examined to clarify the changes in the distribution and composition of the phases from the surface to the unnitrided portion of the specimens, the concentration profiles of nitrogen in the nitrided layers, and the relation between the ion-nitriding temperature and the phase transformation temperature. The formation and growth mechanisms of the nitrided layers will be discussed on the basis of the results obtained.

II. Experimental Procedure

Pure iron commercially available was used. The chemical compositions are given in Table 1. Specimens were cut into the disc of 13 mm in diameter and 8 mm thick. After being polished with #1200 emery paper, the specimens were electropolished in an electrolyte with 80 mass% phosphoric acid and 20 mass% chromic acid,

* This paper was originally published in Japanese in J. Japan Inst. Metals, **54** (1990), 870.

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Table 1 Chemical composition of pure iron used in this work (mass%).

C	Si	Mn	P	S	Cr
0.013	0.25	0.21	0.004	0.014	0.014

and then cleaned in acetone prior to the ion-nitriding.

The experimental procedures and conditions for the ion-nitriding are presented briefly here, since the details have been described in Ref. (12). After the specimen was mounted on the cathode in an ion-nitriding furnace and its vacuum bell-jar was evacuated to 1.3×10^{-3} Pa, a mixed gas of N_2 and H_2 purified to 99.9% was introduced to a few hundred Pa and then d.c. glow discharge plasma was generated. The specimens mounted on the cathode were heated by the ion-bombardment and the nitriding temperature of the specimens was measured with a chromel-alumel thermocouple. The nitriding temperature was calibrated by regarding the temperature at the beginning of the formation of γ phase in the surface nitrided layer as the eutectoid transformation temperature of 863 K. Ion-nitrided specimens were taken out from the furnace within about 30 s and then water cooled, while a few specimens were cooled in furnace under the pressure of the ion-nitriding.

The experimental discharge conditions were as follows: discharge gas; 80 vol% N_2 + 20 vol% H_2 , pressure; 665 Pa, nitriding temperature; 803 K · 923 K · 1013 K, nitriding time; 2.1 ~ 14.7 ks, discharge voltage; 440 ~ 550 V; discharge current density; 50 ~ 80 A/m².

The ion-nitrided specimens were analyzed from the surface toward the unnitrided portion of the specimens by use of an optical microscope, SEM, EPMA, an X-ray diffractometer and a micro-vickers hardness tester. For metallographic examinations of the specimens, an etching solution of 6 mass% ferric chloride-3 mass% hydrochloric acid-91 mass% ethanol was utilized. An averaged nitrogen concentration was estimated from the mass variation of the specimens due to the ion-nitriding.

III. Experimental Results

1. Change in hardness profiles of the surface hardened layers with nitriding temperature

When pure irons are ion-nitrided at 803, 923 and 1013 K for 2.1 ~ 14.7 ks followed by water cooling, the nitrided layers formed are composed of two different layers. One is a surface hardened layer whose hardness varies between Hv 400 and Hv 700, and the other is an inward diffusion layer with a hardness of about Hv 250. Figure 1 shows hardness profiles of the specimens ion-nitrided at these temperatures for 14.7 ks followed by water cooling. As shown in Fig. 1, when nitrided at (a) 803 K, the hardness of the surface hardened layer decreases monotonically from about Hv 700 to about Hv 250 in the diffusion layer. The hardness of the diffusion layer decreases

Fig. 1 Hardness profiles for specimens ion-nitrided at (a) 803 K, (b) 923 K and (c) 1013 K for 14.7 ks.

gradually from about Hv 250 to about Hv 150 in the un-nitrided portion of the specimens. When nitrided at (b) 923 K, the nitrided layer is composed of an outermost hardened layer of about Hv 700 and an inner layer of Hv 350 ~ 400. In this case, the hardness of this inner layer increases to about Hv 500 near the diffusion layer. When nitrided at (c) 1013 K, the hardness increases from about Hv 400 to about Hv 700 toward the inside and then decreases to the hardness of the diffusion layer rapidly. Hence, it is clear that difference in the nitriding temperature results in a considerable variation in hardness profiles of the surface hardened layers, while there is a little change in hardness of each diffusion layer. In this paper, the surface hardened layer means the hardened layer exclusive of the diffusion layer.

The variation in thickness of the surface hardened layers with nitriding time is shown in Fig. 2 at the nitriding temperatures of (a) 803 K, (b) 923 K and (c) 1013 K. The thickness of the surface hardened layers means the distance from the surface to the boundary with the diffusion layer, and it was obtained from metallographic examination of the etched cross-sections of the specimens. (d) in Fig. 2 corresponds to the thickness of the layer nitrided at 923 K in Fig. 1(b) with the hardness of about Hv 700 and it was obtained by the same methods.

2. Analysis of surface hardened layers ion-nitrided at 803 K

Figure 3 shows the structure of the vertical cross-section of the specimen nitrided at 803 K for 14.7 ks observed under an optical microscope. The white banded region at the left in Fig. 3 corresponds to the outermost hardened layer in Fig. 1(a), and, as is mentioned later, it is regarded as a compound layer mainly composed of

Fig. 2 Variation in thickness of the surface hardened layers except the diffusion layers with nitriding time for specimens ion-nitrided at (a) 803 K, (b) 923 K and (c) 1013 K. The dashed line (d) indicates the thickness of the compound layer alone in the hardened case by nitriding at 923 K.

Fig. 3 Microstructure of specimen ion-nitrided at 803 K for 14.7 ks.

γ' -Fe₄N. An adjacent region to the compound layer is a diffusion layer.

The surface of the nitrided specimen was removed step by step by means of electropolishing in an electrolyte with H₃PO₄ and CrO₃ and then X-ray diffraction patterns were taken from the electropolished surfaces at each step using X-ray diffractometer (CoK α radiation, 25 kV-16 mA) in order to identify the phases distributed through the nitrided layers. Figure 4 shows X-ray diffraction patterns taken from the surface layers electropolished by 5–15 μ m of the specimens nitrided at 803 K for 14.7 ks. As shown in Fig. 4, an outermost region of the surface hardened layer is composed of γ' -Fe₄N, ϵ -Fe_{2.3}N and α -Fe of the matrix (Fig. 4(a)) and an inner region is composed of γ' -Fe₄N and α -Fe (Fig. 4(b)–(d)). In the figures of the present paper, γ' -Fe₄N and ϵ -Fe_{2.3}N are described as γ' N and ϵ N, respectively. The decrease in the

Fig. 4 Comparison between X-ray diffraction patterns of electropolished surfaces. The specimens ion-nitrided at 803 K for 14.7 ks were electropolished for (a) 0 μ m, (b) 5 μ m, (c) 12 μ m and (d) 15 μ m.

amount of γ' -Fe₄N of the surface hardened layer toward the inside seems to correspond to the decrease of the vickers hardness shown in Fig. 1(a). In Fig. 5(a), a concentration profile of nitrogen in the specimen nitrided for 14.7 ks measured by EPMA (NK α) is presented. Though these concentration profiles of nitrogen have inherently an error in some degree due to the radial spread of electron beam of about 10 μ m, it can be seen that large amounts of nitrogen are contained in the hardened layer. The nitrogen concentration shown in the vertical axis in Fig. 5 was obtained by the method described in the next section for the nitriding at 923 K. From these values, nitrogen concentration of the compound layer in the specimen nitrided at 803 K was estimated at about 5.5 mass%. As shown in Fig. 5, nitrogen concentration of the diffusion layer is nearly equal to the noise level of NK α radiation, so it is concluded that nitrogen concentration is less than about 0.1 mass% as reported earlier⁽¹³⁾.

3. Analysis of surface hardened layers ion-nitrided at 923 K

Figure 6(a) shows the structure of the cross-section of the specimen nitrided at 923 K for 14.7 ks observed under an optical microscope. The outermost first layer on the left in Fig. 6(a) corresponds to the outermost hardened layer of about Hv 700 in Fig. 1(b). The adjacent light gray layer corresponds to the inner second layer of about Hv 400 in Fig. 1(b). The inner third region corresponds to the diffusion layer. The square marks observed in Fig.

Fig. 5 Concentration profiles of nitrogen in specimens ion-nitrided at (a) 803 K, (b) 923 K and (c) 1013 K for 14.7 ks.

Fig. 6 Microstructures of specimens (a) quenched in water and (b) cooled in furnace after the ion-nitriding at 923 K for 14.7 ks.

6 are indentations of micro-vickers hardness. Figure 7(a) is a typical microstructure of this surface hardened layer observed by SEM. The banded region on the left in this figure corresponds to the first layer in Fig. 6(a) and the adjacent deeply etched banded region corresponds to the second layer in Fig. 6(a).

As is the case of the nitriding at 803 K, the identification of the phases distributed through the nitrided layers was done by analysis of X-ray diffraction patterns taken from the electropolished surface after successive removal of the layers by several microns in thickness. Figure 8 shows the variation in the X-ray diffraction patterns obtained from the surface electropolished successively of the specimens nitrided at 923 K for 14.7 ks. In this figure, the X-ray diffraction patterns of (a)~(c) correspond to the first layer in Fig. 1(b) and Fig. 6(a). In Fig. 8(a) of the outermost part of this layer, γ' -Fe₄N and ϵ -Fe_{2.3}N are formed. In (b) and (c) of the inner part of this layer, it is shown that ϵ -Fe_{2.3}N disappears and ϵ -Fe_xN ($x > 3$)⁽¹³⁾, γ' -Fe₄N and the γ phase co-exist. ϵ -Fe_xN is the nitride

Fig. 7 Scanning electron micrographs of specimens (a) quenched in water and (b), (c) cooled in furnace after the ion-nitriding at 923 K for 14.7 ks.

Fig. 8 Comparison between X-ray diffraction patterns of electro-polished surfaces. The specimens ion-nitrided at 923 K for 14.7 ks were electropolished for (a) 0 μm , (b) 9 μm , (c) 18 μm , (d) 33 μm , (e) 62 μm , (f) 65 μm and (g) 68 μm .

whose nitrogen concentration is lower than $\epsilon\text{-Fe}_{2.3}\text{N}$ and is described as ϵ_x in this figure. The X-ray diffraction patterns of (d) ~ (g) in Fig. 8 correspond to the second layer. In the vicinity of (d), it is composed of the γ phase only, and in the inner part apart from the surface by more than about 60 μm , the diffraction pattern of α phase appears. In this case, the lattice constants of the γ phase were calculated by the Nelson-Riley method from the patterns (d) ~ (g) extended to high diffraction angles. The lattice constants ranged from 0.3640 to 0.3636 nm were obtained, and the values became smaller in a deeper position from the surface. Based upon the relation between the lattice constants and nitrogen concentrations⁽¹³⁾, the averaged nitrogen concentration of the γ phase was estimated at about 2.3 mass%. The striped pattern is observed in the second layer by SEM, as shown in Fig. 7(a), and the hardness of this layer is about Hv 400. In this Fig. 7(a), lenticular martensites are observed near the diffusion layer and the hardness is raised to about Hv 500 near this region.

The concentration profile of nitrogen for the specimen

nitrided at 923 K for 14.7 ks is shown in Fig. 5(b). The outermost region with a high nitrogen concentration corresponds to the compound layer composed of $\gamma'\text{-Fe}_4\text{N}$, etc., and the adjacent plateau corresponds to the γ phase. The innermost region with a nearly constant nitrogen concentration corresponds to the diffusion layer. The values of nitrogen concentration on the ordinate in Fig. 5 were determined by proportional allotment, based on the results that the averaged nitrogen concentration of the γ phase estimated by the lattice constant was about 2.3 mass% and the nitrogen concentration of the diffusion layer was less than about 0.1 mass%⁽¹³⁾.

To clarify the effect of cooling rate from the nitriding temperature on the structures of the surface hardened layers, the furnace-cooled specimen was examined in comparison with the water-cooled specimen. As seen in Fig. 9, it is observed in the furnace-cooled specimens that the compound layer is softened to about Hv 600, the γ phase region near the diffusion layer is hardened slightly and the diffusion layer is softened to about Hv 150 which is nearly equal to the hardness of the unnitrided portion of the specimen. As a whole, the hardness profiles resemble each other.

The structures of cross-sections of the furnace-cooled specimens are shown in Fig. 6(b) examined by an optical microscope and in Fig. 7(b), (c) by SEM. The distinct differences observed in Fig. 6(b) compared with Fig. 6(a) are as follows. As seen in Fig. 6(b), the gray banded markings like as grain boundaries are observed in the outer part of the γ phase and its etching pattern resembles the inner part of the γ phase. It is supposed that the same materials are formed in these parts. At the grain boundaries and within the grains in the diffusion layer, needle-like and granular precipitates are observed and these are supposed to be $\gamma'\text{-Fe}_4\text{N}$ and $\alpha''\text{-Fe}_{16}\text{N}_2$ ⁽⁴⁾⁽¹⁴⁾. For the furnace-cooled specimen, as shown in Fig. 10, the identification of the phases distributed through the nitrided layers was done by the same method as described above. In this figure, the X-ray diffraction patterns of (a) and (b) correspond to the compound layer. Except for small amounts of $\epsilon\text{-Fe}_{2.3}\text{N}$ at the outermost part of this layer, this layer is mainly composed of $\gamma'\text{-Fe}_4\text{N}$ and a small amount of the α phase, and $\epsilon\text{-Fe}_x\text{N}$ is not observed unlike the case of the specimens nitrided followed by water cooling as seen in Fig. 8. The X-ray diffraction patterns (c) ~ (e) correspond to the second inner layer. In this layer, the γ phase is formed, and the α phase and a small amount of $\gamma'\text{-Fe}_4\text{N}$ is also observed. In the case of (c) and (d), a large quantity of the γ phase is formed, but in the case of (e), the amount of the α phase increases considerably and also the amount of $\gamma'\text{-Fe}_4\text{N}$ increases in some degree. From the observations mentioned above, it is supposed that in the γ phase layer formed during nitriding, the γ phase decomposed into the α phase and $\gamma'\text{-Fe}_4\text{N}$ ⁽¹³⁾ at the gray-etched region along the grain boundaries and near the diffusion layer as shown in Fig. 6(b). From SEM observations of the hardened layers as shown in Fig. 7(b) and (c), a considerable amount of lenticular martensites is formed in the region of the γ phase near the diffusion

Fig. 9 Hardness profiles for specimens (a) quenched in water and (b) cooled in furnace after the ion-nitriding at 923 K for 14.7 ks.

layer. The nitrogen concentration of the γ phase in the furnace-cooled specimen was estimated at about 2.1 mass%, utilizing the lattice constant of 0.3635 nm for the γ phase which was obtained from the X-ray diffraction patterns of Fig. 10(d), and this value was smaller than that of the γ phase in the water-cooled specimens. Therefore, in the case of the furnace-cooled specimen, as shown in Fig. 9(b), the increase in hardness at the region of the γ phase near the diffusion layer is due to the formation of martensite and the precipitation of γ' -Fe₄N. The decrease in hardness of the compound layer in the furnace-cooled specimen seen in Fig. 9(b) is mainly attributed to the considerable decrease in nitrogen concentration, estimated at about 4.3 mass% by EPMA analysis, compared with the water-cooled specimen. The reason why the hardness of the diffusion layer decreased to the hardness of an untreated parent material may be due to the precipitation of nitrogen from solid solution as nitrides during the cooling in furnace as shown in Fig. 6(b).

4. Analysis of surface hardened layers ion-nitrided at 1013 K

Figure 11 shows the structure of the cross-section of the specimen nitrided at 1013 K for 14.3 ks followed by water cooling, observed by an optical microscope. It can be seen that lenticular martensites are formed in the nitrided layer.

For this specimen, as shown in Fig. 12, the identification of the phases distributed through the nitrided layers was done using the electropolishing technique described

Fig. 10 Comparison between X-ray diffraction patterns of electropolished surfaces. The specimens cooled in furnace after ion-nitriding at 923 K for 14.7 ks were electropolished for (a) 0 μ m, (b) 8 μ m, (c) 30 μ m, (d) 50 μ m and (e) 60 μ m.

Fig. 11 Microstructure of specimen ion-nitrided at 1013 K for 14.7 ks.

above. In Fig. 12, at the outermost layer (a), small amounts of γ' -Fe₄N and ϵ -Fe_xN ($x > 3$) are observed, but the portion between (b) and (f) is composed of the γ and α' phases, only. The reason why the term of the α' phase is used instead of the α phase is that the half width of the diffraction peak of this phase is broad and the structure

Fig. 12 Comparison between X-ray diffraction patterns of electropolished surfaces. The specimens ion-nitrided at 1013 K for 14.7 ks were electropolished for (a) 0 μm , (b) 11 μm , (c) 28 μm , (d) 51 μm , (e) 68 μm and (f) 78 μm .

of martensite is observed as seen in Fig. 11. The ratio of the γ phase to the α' phase decreases toward the inside from (b) to (f), and inversely, the hardness of the nitrided layer increases from about Hv 400 to about Hv 700 in the hardness profile of Fig. 1(c). The lattice constants of the γ phase decreases from 0.3633 to 0.3606 nm toward the inside, so averaged nitrogen concentration for the region from (c) to (d) in Fig. 12 was estimated at about 1.5 mass%.

The nitrogen concentration profile of the specimen nitrided for 14.7 ks is shown in Fig. 5(c). Nitrogen decreases gradually in plateau stage and the nitrogen concentration on the ordinate of curve (c) coincident with the averaged nitrogen concentration of about 1.5 mass% of the second layer as mentioned above. The averaged nitrogen concentration of the surface hardened layer was estimated at 1.6 mass% from the mass variation of the specimen during nitriding assuming that nitrogen concentration was not changed in the surface hardened layer and decreased in the diffusion layer along the form of error function from the solid solution limit of nitrogen of about 0.06 mass%⁽¹³⁾ in α -Fe at 1013 K. The value of 1.6 mass% is close to 1.5 mass% as mentioned above. It should be considered here that the method for the estimation of nitrogen concentration making use of the lattice constant of the γ phase was reasonable.

IV. Discussion

As described above, it was found that the surface hardened layers and diffusion layers were formed peculiar to the nitriding temperatures and cooling rates. The formation mechanisms of these layers will be discussed along this line.

In the case of the nitriding at the temperature of 803 K, as is well-known, the compound layer mainly composed of γ' -Fe₄N is formed in an outermost layer, and the diffusion layer is developed in an inner layer. In the case of the nitriding at 923 K, the compound layer with a high nitrogen concentration is formed in an outermost layer, and the γ phase with a nitrogen concentration of about 2.3 mass% is formed in an inner second layer. The reason for the formation of γ phase may be explained by an iron-nitrogen phase diagram⁽¹³⁾. This is to say, the A_3 temperature is lowered considerably by the addition of nitrogen, and the eutectoid transformation temperature comes to 863 K at the nitrogen concentration of 2.35 mass%⁽¹³⁾. At nitriding temperature of 923 K, nitrogen of averaged concentration of about 2.3 mass% is dissolved in solid solution and that point in Fe-N phase diagram is in the γ phase region. It is supposed here that γ phase is formed through the reverse phase transformation of the α to γ phase. When this specimen is water cooled from its nitriding temperature, that γ phase is still stable at a room temperature on the account that the M_s point of Fe-N phase diagram is below a room temperature at the nitrogen concentration more than about 2.2 mass%, as reported in Ref. (15). The M_s temperature is estimated at 263 ± 40 K for a nitrogen concentration of about 2.3 mass%. On the other hand, in the case of the specimen nitrided at 923 K followed by furnace cooling, γ phase is formed similarly during nitriding, but γ phase decomposes into γ' -Fe₄N and α phase in the vicinity of grain boundaries and the neighborhood of the diffusion layer during furnace cooling and then γ phase with averaged nitrogen concentration of about 2.1 mass% is retained. As in the furnace-cooled specimen, the nitrogen concentration is smaller than that in the water-cooled specimen, plenty of martensite is formed near the diffusion layer.

In the case of the specimen nitrided at 1013 K followed by water cooling, it is considered to be difficult to form the compound layer because of the decomposition of γ' -Fe₄N above about 953 K⁽¹³⁾ and the denitrogenization⁽¹⁶⁾, so only small amounts of γ' -Fe₄N and ϵ -Fe_xN are formed in the outermost layer as shown in Fig. 12 (a). As seen in the concentration profile of nitrogen of Fig. 5(c), the nitrogen concentration in the γ phase decreases from about 2 mass% near the surface to about 1 mass% near the diffusion layer. According to Fe-N diagram⁽¹³⁾, the nitrogen concentration at A_3 temperature of 1013 K is about 0.8 mass%, and it is presumed that γ phase exists near at the diffusion layer during nitriding. When this specimen is water cooled, Fe-N martensite is formed, because nitrogen concentration of this second layer is less than about 2.2 mass%⁽¹⁵⁾ at which concentration the M_s point lies near room temperature. Increasing in the

amount of martensite toward the inside of the specimens results in the hardness profile as shown in Fig. 1(c). In this case, the M_s temperature which corresponds to the averaged nitrogen concentration of about 1.5 mass% for this second layer is estimated at 398 ± 40 K⁽¹⁵⁾.

As mentioned above, in the case of the nitriding temperature lower than eutectoid transformation temperature of 863 K such as the case of 803 K nitriding, the nitrided layer composed of a compound layer and a diffusion layer is formed. On the other hand, in the case of the nitriding temperature higher than eutectoid transformation temperature such as in the case of 923 and 1013 K nitridings, the γ phase with a nitrogen concentration more than those determined by A_3 points corresponding to the nitriding temperatures is formed in the upper portion of the diffusion layer during nitriding and this γ phase grows up with the nitriding time. It is considered here that, during cooling, the grown-up γ phase is retained or transformed into martensite depending on the M_s temperature which varies with nitrogen concentration.

V. Conclusions

Pure irons commercially available were ion-nitrided at 803, 923 and 1013 K for 2.1 ~ 14.7 ks in a mixed gas (80 vol% N_2 + 20 vol% H_2) under a reduced pressure of 665 Pa followed by water cooling, while partly furnace cooled. The characterized surface hardened layers were formed depending upon the nitriding conditions. The following results are obtained.

(1) When nitrided at 803 K followed by water cooling, the nitrided specimen surface consists of; (i) a compound layer of about Hv 700 which is mainly composed of γ' -Fe₄N, and (ii) a diffusion layer of about Hv 250.

(2) When nitrided at 903 K followed by water cooling, the nitrided specimen surface consists of; (i) a compound layer of about Hv 700 which is mainly composed of γ' -Fe₄N, (ii) an inner layer of the γ phase of about Hv 400 with an averaged nitrogen concentration of about 2.3 mass% and the thickness of less than twice as that of the compound layer, and (iii) a diffusion layer.

(3) When nitrided at 923 K followed by furnace cooling, the γ phase formed during nitriding decomposes into γ' -Fe₄N and α phase at the region of grain boundaries and the neighborhood of the diffusion layer in the γ phase during the furnace cooling. The lenticular martensites are observed near the diffusion layer in the retained austenite accompanied with the increase in hardness. The hardness of the diffusion layer became nearly equal with that of the material untreated owing to the precipitation

of needle-like nitrides.

(4) When nitrided at 1013 K followed by water cooling, the nitrided specimen surface consists of; (i) a thin compound layer, (ii) an inner hardened layer composed of γ and α' martensite with an averaged nitrogen concentration of about 1.5 mass%, of which the hardness increases from Hv 400 to Hv 700 toward the inside, corresponding to the increase of the amount of the α' phase, and (iii) a diffusion layer.

(5) In the case of the nitriding at 923 K and 1013 K, the γ phase was formed at a nitrogen concentration determined by the Fe-N phase diagram. On nitriding at 923 K, the γ phase was retained even at a room temperature and on nitriding at 1013 K, the γ phase was transformed to α' phase. The result can be well explained in terms of the correlation between the nitrogen concentration and M_s point.

Acknowledgments

The present author is thankful to Prof. T. Maki and Prof. R. Ootani, of Faculty of Engineering, Kyoto University, and to Prof. K. Kamachi of Faculty of Science and Technology, Kinki University, for helpful discussions.

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