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# Plasma Nitriding Behavior on Surface Hardening of Copper-Contained High Tensile Steel†

Shuvra MAJUMDER\*, Kazuhiro NAKATA\*\* and Masao USHIO\*\*\*

## Abstract

Plasma nitriding effects on high tensile steel containing 0.006%C, 0.29%Si, 1.34%Mn, 1.18%Cu, 1.46%Ni, 0.62%Cr, and 0.44%Mo in mass% have been investigated at different nitriding times and temperatures from 500 °C to 640 °C and up to 4 hours. Hardness profiles on cross sections of nitrided layers were measured to determine the case hardening depth along with the surface hardness. Optical micrograph and X-ray diffraction analyses revealed two nitrided layers. The first layer is a compound layer comprised of two nitrides,  $\gamma$ -Fe<sub>4</sub>N and  $\epsilon$ -Fe<sub>2-3</sub>N and the second layer is a diffusion layer below it. The surface hardness of the nitrided layer reached 700 to 800 HV due to the nitride compound layer. The hardness of the diffusion layer reached about 650 HV just below the compound layer and decreased gradually to substrate hardness inwards. The hardening of the diffusion layer is believed to be due to the precipitation hardening of nitrides. The thickness of the nitrided layer, that is the hardened layer, increased with increasing temperature up to about 500  $\mu$ m including a thin compound layer less than 10  $\mu$ m. Growth kinetics was also discussed.

**KEY WORDS:** (Plasma nitriding) (Surface hardening) (Microhardness) (Nitride) (Iron-nitride) (Activation energy) (High tensile steel)

## 1. Introduction

High tensile steel is mainly used for structural purposes. High load capacity and corrosion resistance both are highly desired for high tensile steel. The application of nitriding will provide the possibility of high surface hardness with increased case depth. Stable precipitated nitrides can retain the hardness of the surface area even at high temperature. Thus, nitriding will provide new opportunities for high tensile steel in addition to structural applications. There are many studies of plasma nitriding of plain carbon and low alloyed carbon steels. However, plasma nitriding of high tensile steel has not been studied before, because there was no strong requirement for surface hardening of this type of steel before. The purpose of this study was to investigate the plasma nitriding behavior of high tensile steel at various temperatures. Surface hardness, case depth, growth kinetics of the nitrided layer, X-ray diffraction and microstructural analyses have been carried out.

## 2. Experimental Procedure

### 2.1 Specimen preparation

The specimen used for nitriding was a block of size 10 mm x 10 mm x 20 mm. Specimens were heated at 1200 °C for 1h for solution heat treatment followed by water quenching and then ground with #320 emery paper to eliminate the surface contaminated layer. The chemical composition of the specimens used is given in Table 1.

### 2.2 Nitriding procedure

The plasma nitriding system used in this investigation is a conventional DC glow discharge type, details of which have been reported elsewhere<sup>1)</sup>. Plasma nitriding was performed in a N<sub>2</sub>+H<sub>2</sub> gas mixture with equal volume ratios of N<sub>2</sub> and H<sub>2</sub>. Prior to nitriding, the specimen was degreased with acetone and dried, and it was placed on the specimen holder as a cathode and the chamber was evacuated to about 6.65Pa. After the desired vacuum had been reached, the treating gas was introduced into the system. The pressure inside the chamber was maintained at 532Pa. The discharge voltage and current

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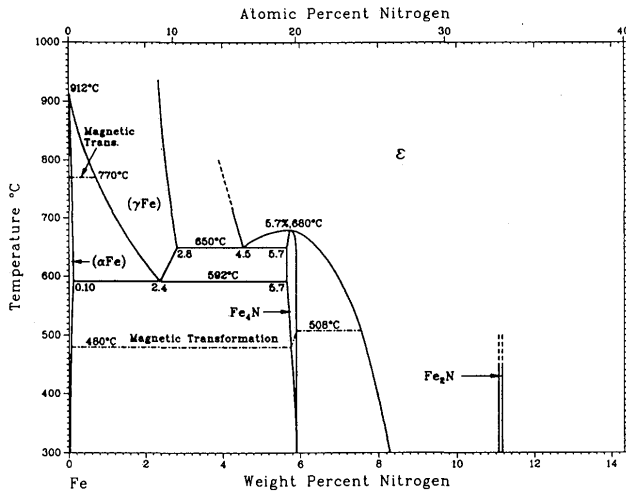
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**Table 1** Chemical composition of copper-contained high tensile steel used (mass%).

| C     | Si   | Mn   | P     | S     | Cu   | Ni   | Cr   | Mo   | Fe   |
|-------|------|------|-------|-------|------|------|------|------|------|
| 0.006 | 0.29 | 1.34 | 0.005 | 0.002 | 1.18 | 1.46 | 0.62 | 0.44 | Bal. |



**Fig.1** Fe-N binary alloy phase diagram.

were gradually increased to reach the desired temperature. After nitriding for a specified time at the desired temperature, each specimen was cooled for about 30 minutes in a stream of the treating gas. In the Fe-N system eutectoid reaction appears at 592°C as shown in **Fig.1**<sup>2)</sup>. Therefore, nitriding temperatures were selected at 500, 550 and 580°C as a sub-eutectoid temperature and, 610 and 640°C above the eutectoid temperature for different nitriding times, 1, 2 and 4h each.

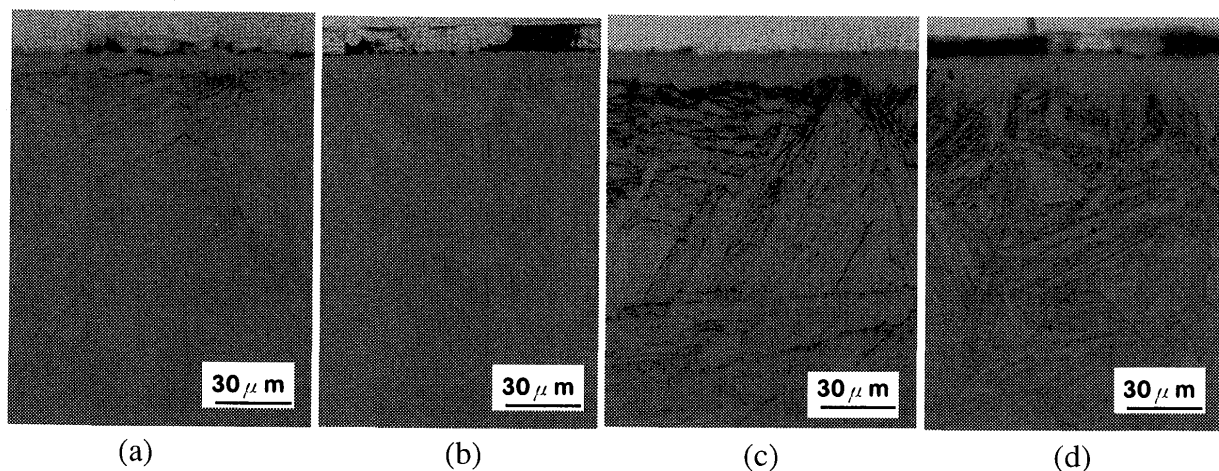
## 2.3 Metallography

For measurement of the penetration distance profiles, thickness of compound layer and diffusion layer, transverse microsections of nitrided samples were taken and mounted in epoxy resin, ground by #320 to #1200 emery papers and fine polished by diamond paste. Samples were then etched for 8-10s in 3% alcoholic nitric acid to reveal the structure. Microhardness testing with a 0.49N load was used to measure the penetration distance profiles from surface to diffusion layer. From the result of hardness profiles the variation of case depths with time was also measured to establish the thickness of the diffusion layer.

## 3. Result and Discussion

### 3.1 Microstructure

Microstructural changes occurred in the high tensile steel during plasma nitriding were observed by optical microscope. The microstructure of the nitrided specimens is presented in **Figs.2** and **3** at nitriding time of 1 and 4h respectively. The white layer at the top surface is a compound layer consisting of two iron nitrides, mainly  $\gamma'$ -Fe<sub>4</sub>N and partly  $\epsilon$ -Fe<sub>2-3</sub>N by the results of X-ray diffraction analysis as shown in **Fig.4**. No other nitride was detected. **Figure 5** shows the relation between the thickness of the compound layer and nitriding temperature



**Fig.2** Optical micrographs of cross-sections of the nitrided layer nitrided for 1h, (a) 550°C, (b) 580°C, (c) 610°C, (d) 640°C.

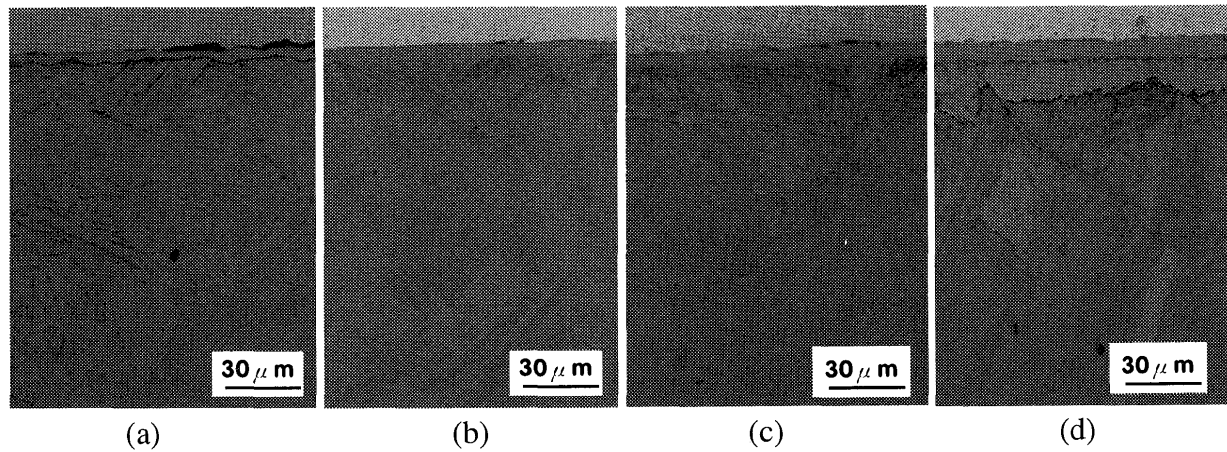


Fig.3 Optical micrographs of cross-sections of the nitrided layer nitrided for 4h, (a) 550°C, (b) 580°C, (c) 610°C, (d) 640°C.

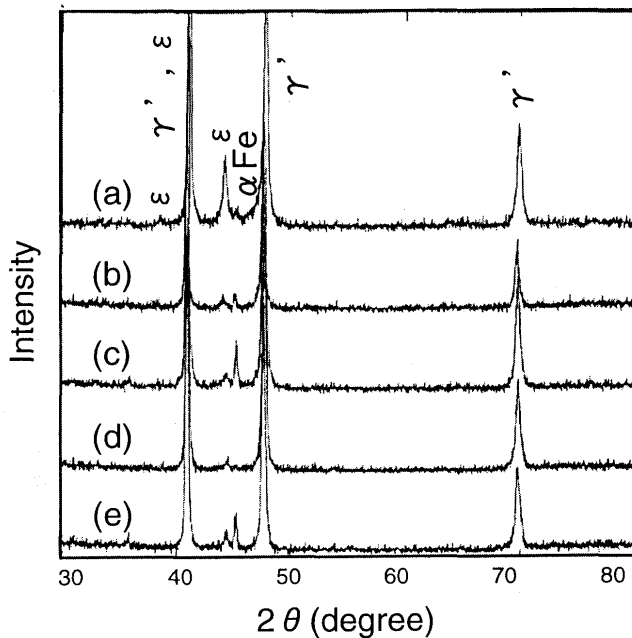


Fig.4 X-ray diffraction pattern of the steels nitrided for 2h at (a) 500°C, (b) 550°C, (c) 580°C, (d) 610°C, (e) 640°C.

for each nitriding time. With increasing temperature the thickness of the compound layer increases. Above the eutectoid temperature, however, the thickness of the compound layer was a maximum and then slightly decreased. It is apparent that above the eutectoid temperature of the Fe-N system, the diffusion coefficient of nitrogen becomes low due to formation of austenite,  $\gamma$ -Fe. Above the eutectoid temperature (592°C), therefore, a black layer was formed below the white layer as is well shown in Fig.2(c). This black layer is called braunite, eutectoid consisting of  $\gamma'$ -Fe<sub>4</sub>N and ferrite,  $\alpha$ -Fe as shown in Fig.1.

### 3.2 Surface hardness

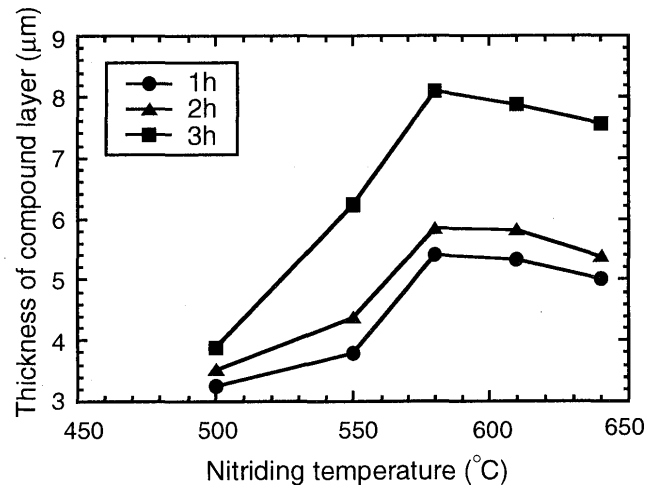


Fig.5 Effect of nitriding temperature on thickness of compound layer.

Figure 6 shows the relation between surface hardness of a nitrided specimen and nitriding temperature. After nitriding, surface hardness of the specimen increased remarkably to 700 to 800 HV compared with a substrate hardness of about 300 HV. With increasing temperature, surface hardness is gradually increased up to at 610°C and after this, decreased sharply as shown in Fig. 6. It is well known that surface hardness depends not only on the hardness of the compound layer but also on its thickness. However, the thickness of the compound layer is almost the same above 580°C and the compound layer consisted dominantly of  $\gamma'$ -Fe<sub>4</sub>N irrespective of nitriding temperature. These facts suggest that the hardness of the compound layer itself decreased at 640°C. Coarsening of nitride grain size or the decrease of strain in nitride may explain this.

In this study, it was difficult to measure the hardness of the compound layer itself in its cross-section due to its thin-ness (less than 10μm).

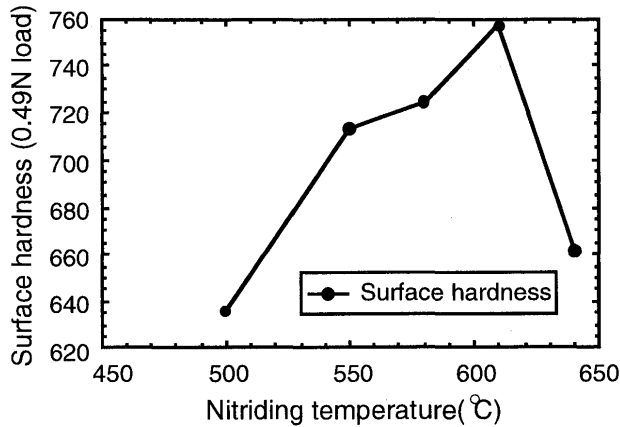


Fig.6 Effect of nitriding temperature on surface hardness when nitrided for 2h

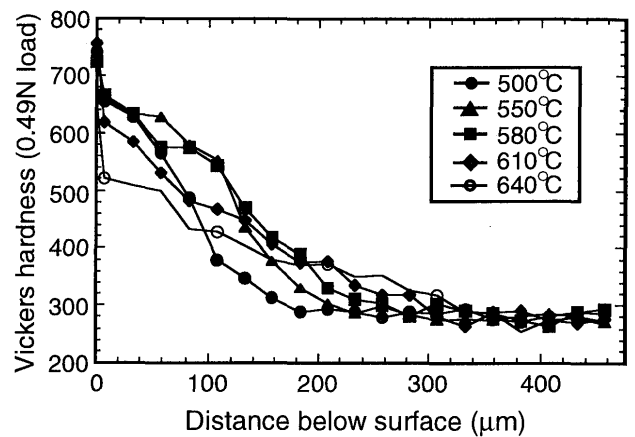


Fig.8 Variation in hardness vs. penetration distance profiles with nitriding temperature for 2h.

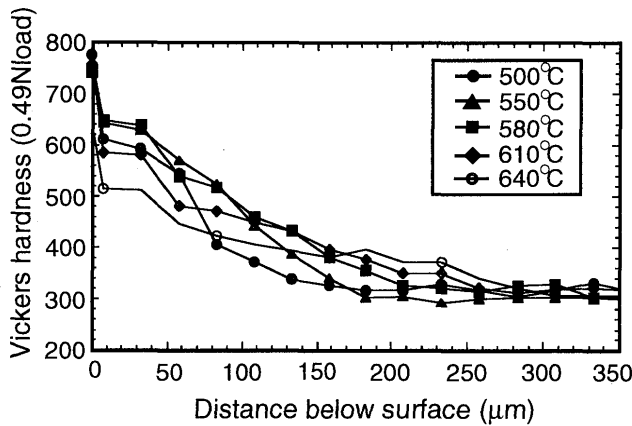


Fig.7 Variation in hardness vs. penetration distance profiles with nitriding temperature for 1h.

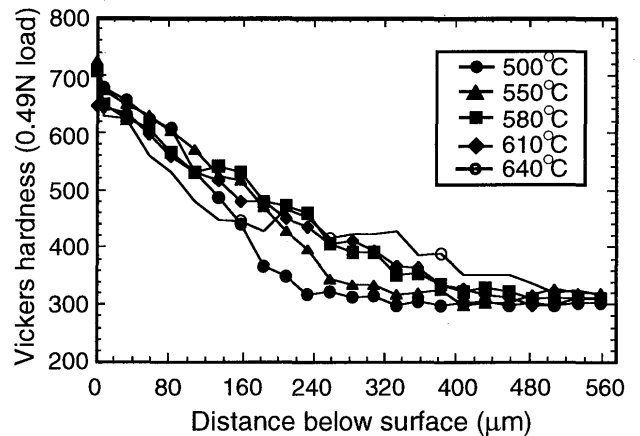


Fig.9 Variation in hardness vs. penetration distance profiles with nitriding temperature for 4h.

### 3.3 Hardness profiles in cross-section

Figures 7, 8 and 9 show hardness profiles in cross-sections for each nitriding time, 1, 2, and 4h respectively, where surface hardness is plotted on the vertical axis in each figure. It can be seen that the case depth, namely the thickness of the hardened layer increased with increasing temperature. This corresponds to diffusion penetration of nitrogen as is well known. The surface hardness of the nitrided layer depends on the nitride compound layer as mentioned in 3.2.

The hardness of the diffusion layer below the compound layer reached about 650 HV and decreased gradually to the core hardness inward. Moreover, the hardness of the diffusion layer increased gradually with increasing nitriding temperature up to 580°C, but, after this, with increasing nitriding temperature it decreased.

The hardening of the diffusion layer is believed to be due to the precipitation hardening of nitrides, caused by finely dispersed nitrides within the matrix containing nitrogen diffused from the specimen surface. Phillips and Seybolt<sup>3)</sup> studied the precipitation of alloy nitrides using

electron microscopy, and noted that coarse nitrides caused small to moderate hardening. They identified fine particles, which were hard to resolve, to be the principal source of hardening in nitriding. Theoretically, it can be envisaged that at the lowest temperature the nitrogen uptake and precipitate density are low and as a result the degree of hardening is also low. At higher temperatures and/or longer treatment times, both precipitate growth and tempering of the matrix become important.

It has been observed in many precipitation hardening alloys that a maximum in hardness is achieved at a particular temperature and time. This hardness is in turn related to both precipitate density and precipitate size. Similar relationships were confirmed by TEM observation in plasma nitriding hardening of Ni-base binary alloys<sup>4)</sup>. Therefore, with regard to the nitriding of high tensile steel in this study, it was estimated that near to 580°C a nitriding temperature for optimum nitride precipitate size and density is produced. Also, at high temperatures the matrix continues to temper and soften, and as a result the hardness of the case is reduced. At

higher temperatures and longer treatment times a decrease in hardness, but an increase in the case depth occurred in all the conditions in this study, which is also consistent with the other observations<sup>5, 6</sup>. The size and stability of the precipitated nitrides mainly determines the development of the hardness profiles.

Therefore, hardness-depth curves that were observed in this study, can be characterized by a smooth transition from near the surface (excluding the surface hardness) to the core. Apparently, this behavior is a result of strong interaction between the alloying elements (0.62%Cr, 0.44%Mo and 1.34%Mn) present in the high tensile steel. Among them Cr is well-known as a nitride precipitation former. However, it was not possible to identify the presence of alloy nitrides by X-ray diffraction techniques in this case.

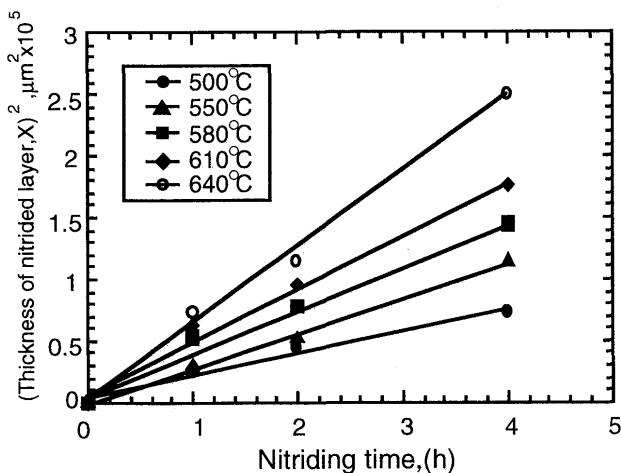
### 3.4 Growth rate of nitrided layer

Based on the systematic variation of the nitriding time and temperature parameters, the growth kinetics of the nitrided layer were investigated. In this study, the nitrided layer is considered as a combination of both the compound layer and the diffusion layer. It is apparent that the nitrided layer grows parabolically with time. According to the parabolic rate law formula, it can be written that

$$X^2 = (K_p)t \quad (1)$$

Where  $X$  is the case depth,  $K_p$  is the parabolic rate constant and  $t$  is the nitriding time.

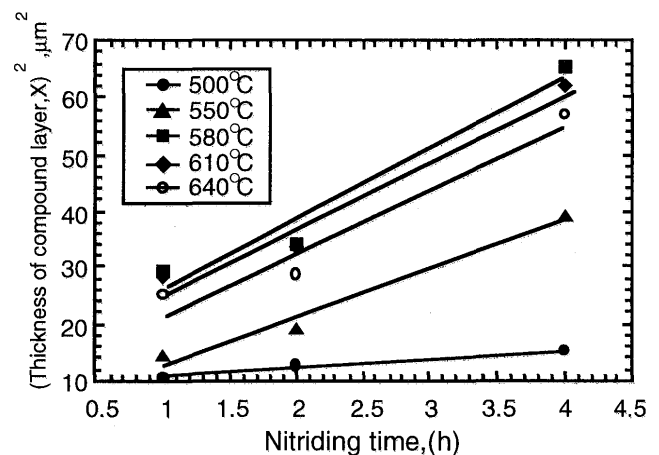
**Figures 10 and 11** are plotted where the square of the case depth,  $X^2$  is a function of nitriding time,  $t$ . Figs.10 and 11 are drawn for the nitrided layer and the compound layer respectively. A linear relationship between the square of the case depth and nitriding time was obtained in each figure. These show that the nitriding



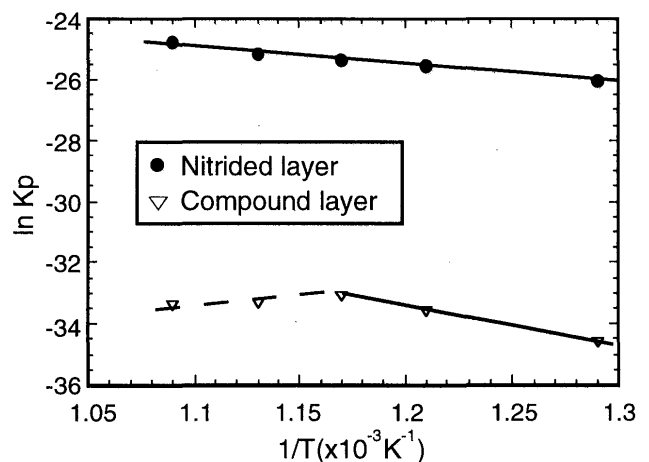
**Fig.10** Relation between square of nitrided layer thickness and nitriding time.

process is controlled by the volume diffusion of nitrogen in steel.

The logarithm of rate constants obtained from Figs.10 and 11 is drawn as a function of nitriding temperature in **Fig.12**, which shows a typical Arrhenius plot. A linear relationship was obtained for the nitrided layer, but in case of the compound layer a deviation from a linear relationship was observed over the eutectoid temperature range due to the decrease in  $K_p$  values. This decrease was caused by the formation of austenite,  $\gamma$ -Fe, during nitriding treatment above the eutectoid temperature due to the decrease in the nitrogen diffusion coefficient in austenite as compared with that in ferrite,  $\alpha$ -Fe. However, there was no such effect observed in the case of the nitrided layer. This may be due to the much lower nitrogen concentration in the diffusion layer, in which, even over eutectoid temperature, the formation of  $\gamma$ -Fe is still small according to Fe-N phase diagram as shown in Fig.1



**Fig.11** Relation between square of compound layer thickness and nitriding time.



**Fig.12** Relation between  $\ln K_p$  and reciprocal nitriding temperature for nitrided layer and compound layer.

An activation energy (Q) of 75KJ/mole is calculated for the growth of the nitrided layer. In the Metals Handbook, the activation energy for the diffusion of nitrogen in  $\alpha$ -Fe is 81.49 to 81.72 KJ/mol in this nitriding temperature range<sup>7)</sup> and 157 KJ/mol at more than 950°C in  $\gamma$ -Fe<sup>7)</sup>. The obtained value, 75KJ/mole is near to that in  $\alpha$ -Fe. In comparison, the activation energy for the diffusion of nitrogen in low carbon steel below eutectoid temperature is around 81.88KJ/mole<sup>8)</sup>. In addition, the activation energy in Fe-Al-Mn-Cr-C alloys at 1000-1100°C is 63-109KJ/mole<sup>9)</sup>.

The activation energy is also calculated on the basis of the compound layer at lower temperature range than the eutectoid temperature, which is 153KJ/mole, much higher than that for the nitrided layer.

## 4. Conclusion

Plasma nitriding of high tensile steel containing 0.006%C, 0.29%Si, 1.34%Mn, 1.18%Cu, 1.46%Ni, 0.62%Cr, and 0.44%Mo in mass% has been investigated at different nitriding times and temperatures from 500°C to 640°C up to 4 hours. Conclusions obtained are as follow:

- (1) Nitrided layer consisted of two layers. The first layer was a compound layer comprised of two nitrides, mainly  $\gamma$ -Fe<sub>4</sub>N and partly  $\epsilon$ -Fe<sub>2-3</sub>N and the second layer was a diffusion layer below it.
- (2) The surface hardness of the nitrided layer reached 700 to 800 HV due to the nitride compound layer. The hardness of the diffusion layer reached about 650 HV just below the compound layer and decreased gradually to core hardness inward. The hardening of the diffusion layer was believed to be due to the precipitation hardening of nitrides.

- (3) The thickness of the nitrided layer, increased with increasing temperature up to about 500  $\mu$ m including thin compound layer less than 10  $\mu$ m.
- (4) Parabolic growth in the thickness of the layer was observed both for the nitrided layer and the compound layer.
- (5) Parabolic growth rate of the nitrided layer increased with increasing nitriding temperature, but that of the compound layer increased up to 580°C and then decreased slightly above the eutectoid temperature.
- (6) Activation energy obtained for the growth of the nitrided layer was 75 KJ/mol and that for the compound layer was 153 KJ/mol below the eutectoid temperature.

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